

THE FINE STRUCTURE
OF
CONDENSED RING COMPOUNDS

NEIL CAMPBELL

THE STRUCTURE OF NAPHTHALENE, HYDRINDENE, AND TETRALIN DERIVATIVES

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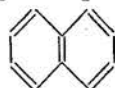
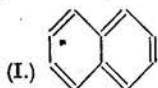
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231. *The Structure of Naphthalene, Hydrindene, and Tetralin Derivatives.*

By (Miss) N. McLEISH and NEIL CAMPBELL.

THE structure of naphthalene has been the subject of many critical investigations, and has recently been attacked from several different standpoints (Challenor and Ingold, J., 1923, **123**, 2066; Obermiller, *J. pr. Chem.*, 1930, **126**, 257; Bell, J., 1932, 2732; Fieser and Lothrop, *J. Amer. Chem. Soc.*, 1935, **57**, 1459; 1936, **58**, 2050; Sidgwick and Springall, J., 1936, 1532; Ufimzew, *Ber.*, 1936, **69**, 2188; Baker and Carruthers, this vol., p. 479). The problem cannot be regarded as solved, for, while Ufimzew (*loc. cit.*) concludes that a modification of the Erdmann formula (*Annalen*, 1893, **275**, 191)—an equilibrium between structures (I), (II), and (III)—affords the most satisfactory explanation of the properties of naphthalene derivatives (cf. Pauling and Wheland, *J. Chem. Physics*, 1933, **1**, 362), most of the evidence supports Fieser and Lothrop's conclusion (*loc. cit.*) that the Erlenmeyer formula (II) is the most acceptable to chemists. The chemical evidence rests chiefly on the reactivity of the 1-position and the non-reactivity of the 3-position in 2-substituted

naphthalene compounds. This is explained by the presence of a double bond between C_1 and C_2 , and a single bond between C_2 and C_3 . Many of the reactions used in the past, however, do not provide convincing proof of the formula, as they are not necessarily dependent on the presence of double bonds. For instance, the isolation of 5:6-benzoquinoline as the sole product of the Skraup reaction with β -naphthylamine (Knueppel, *Ber.*, 1896, 29, 708), though showing the marked reactivity of the 1-position, does not necessarily mean that this is caused by a double bond between C_1 and C_2 . Such reactions are useful as indications,



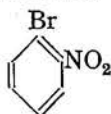
(II.)



(III.)

but must not be taken as conclusive evidence. It is therefore very desirable that the properties and reactions used in such investigations should be known to involve one or more double bonds. For this reason the investigations of Baker and Carruthers (*loc. cit.*) and Fieser and Lothrop (*loc. cit.*) provide the best evidence so far advanced for the arrangement of the double bonds in condensed aromatic compounds. The present paper gives further evidence on somewhat similar lines for the structure of derivatives of naphthalene, hydrindene, and tetralin.

Fuson (*Chem. Reviews*, 1935, 16, 1) in his theory of vinylogy has pointed out that the influence of one functional group on another is observed not only in cases such as nitromethane but also when the groups are separated by carbon atoms linked by a double bond or a system of conjugated double bonds. For example, the mobility of the bromine atom in *o*- and *p*-bromonitrobenzene is due to the presence in the ring of a double bond and two conjugated double bonds, just as the reactivity of the methyl group in nitromethane is also found in *o*- and *p*-nitrotoluene.

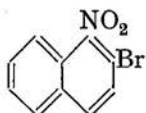


The reactivity of the bromine atom in aromatic bromonitro-compounds is therefore a method for detecting both the presence and the position of double bonds in aromatic compounds, and we have applied the method to bromonitro-derivatives of naphthalene, hydrindene, and tetralin. An analogous method was used by Mills and Smith (*J.*, 1922, 121, 2724) in the quinoline and isoquinoline series. Our work, like that of Fieser and Lothrop (*loc. cit.*) and Baker and Carruthers (*loc. cit.*), has the advantage that it overcomes the objections of Sutton and Pauling (*Trans. Faraday Soc.*, 1935, 31, 939). It has also the advantage that semi-quantitative measurements can readily be made, and the reaction can be performed under mild conditions. The reactivity measurements were made by the piperidine method (cf. Le Fèvre and Turner, *J.*, 1927, 1113), which proved to be the most suitable for the small quantities of compounds which were sometimes at our disposal. The measurements make no claim to accuracy, but are sufficient to show the relative reactivities of the bromine atom in the compounds examined. The results are in the table, and the details of the measurements in the experimental section.

	Percentage removal of bromine.			Percentage removal of bromine.	
	0.5 Hour.	20 Hours.		0.5 Hour.	20 Hours.
1-Bromo-2-nitronaphthalene	91	101	2-Chloro-1-nitronaphthalene ...	46	—
2-Bromo-1-nitronaphthalene	65	100	4-Chloro-1-nitronaphthalene ...	43	—
4-Bromo-1-nitronaphthalene	60	98	8-Chloro-1-nitronaphthalene ...	—	0
5-Bromo-1-nitronaphthalene	—	0	4-Bromo-5-nitrohydrindene ...	—	<5
6-Bromo-2-nitronaphthalene	0	0	6-Bromo-5-nitrohydrindene ...	—	72
5:8-Dibromo-1-nitronaphthalene	0	0	6-Bromo-7-nitrotetralin	5	51
3-Bromo-2-nitronaphthalene	0	0	6-Bromo-5-nitrotetralin	0	0
1-Chloro-2-nitronaphthalene	51	—			

If the Erlenmeyer formula is correct, the bromine atom in 1-bromo-2-nitronaphthalene,

2-bromo-1-nitronaphthalene, and 4-bromo-1-nitronaphthalene should be reactive, and in the other naphthalene compounds it should be non-reactive. The same applies to the corresponding chloronitro-compounds. If, on the other hand, the equilibrium formula of Erdmann ($I \rightleftharpoons II \rightleftharpoons III$) is correct, or an equilibrium between the structures (I) and (III) or (I) and (II) is accepted, 3-bromo-2-nitronaphthalene also must be reactive. In the naphthalene compounds studied (see table) a double bond exists between C_1 and C_2 , and a single bond between C_2 and C_3 . This rules out the equilibrium formulæ given above and



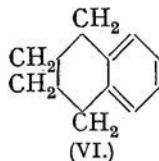
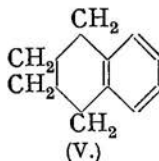
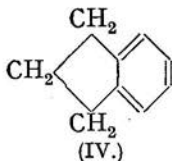
confirms the Erlenmeyer formula. It is possible that the introduction of polar groups such as nitro- and bromo-groups into the naphthalene molecule, which is undoubtedly symmetrical (Kohlräusch, *Ber.*, 1935, **68**, 893), produces an unsymmetrical formula (Ufimzew, *loc. cit.*; Lesser, Kranepuhl, and Gad, *Ber.*, 1925, **58**, 2109) such as that inset, but the parallelism of our results with those of Fieser and other workers is strong evidence for the Erlenmeyer formula.

It might be expected that 6-bromo-2-nitronaphthalene would contain reactive bromine, as the bromine and the nitro-group are separated by a conjugated system of three double bonds. The fact that no reactivity was observed is another proof that the double bond shared by the two rings does not function normally. 8-Chloro-1-nitronaphthalene and 5:8-dibromo-1-nitronaphthalene also are of interest. In these compounds no reactivity was observed, although each contains a halogeno- and a nitro-group ortho to one another. It is clear that mere proximity of the groups is not sufficient to produce reactivity, and this fact confirms the correctness of Fuson's theory.

It must be stressed that all the chemical evidence for the structure of naphthalene rests on the properties and reactions of substituted naphthalene compounds. It is therefore possible that the polar effects of the substituents must be taken into account and what holds for one type of compound may not apply to others or to naphthalene itself. Thus the results of Baker and Carruthers (*loc. cit.*), as suggested by the authors themselves, may indicate in certain compounds an unsymmetrical distribution of bonds due to chelation between the substituents. Similarly there may be displacement of the double bonds by the use of vigorous conditions or reagents. This would account for the formation of 5:6-tetrahydrobenzindan-1-one from β -2-tetrahydronaphthylpropionyl chloride in presence of aluminium chloride (Darzens and Lévy, *Compt. rend.*, 1935, **201**, 902) and the formation of 2-hydroxy-3-naphthoic acid (Schmitt and Burkard, *Ber.*, 1887, **20**, 2702) by the action of carbon dioxide on sodium β -naphthoxide at a high temperature. The question of the mobility of the double bonds in naphthalene compounds can therefore only be settled by a thorough study of the reactions and properties of different types of naphthalene derivatives.

Attempts were made to prepare 8-bromo-1-nitronaphthalene in the same way as the chloro-compound, *i.e.*, action of the halogen on 1-nitronaphthalene, but 5-bromo-1-nitronaphthalene was invariably obtained. This may be due to an isomeric change caused by the hydrobromic acid liberated during the bromination converting the 8-bromo-1-nitronaphthalene first formed into the 5-bromo-compound in the same way that 1:8-dichloronaphthalene is converted into 1:5-dichloronaphthalene by the action of hydrochloric acid (Armstrong and Wynne, *P.*, 1896—97, **13**, 154). For reactivity measurements 5:8-dibromo-1-nitronaphthalene and 8-chloro-1-nitronaphthalene were therefore used instead of 8-bromo-1-nitronaphthalene.

We also applied our methods to derivatives of hydrindene and tetralin. The work of Mills and Nixon (*J.*, 1930, 2510) indicated that in hydrindene and tetralin the bonds were



stabilised, and formulæ (IV) and (V) were advanced. Recent work by Fieser and Lothrop (*loc. cit.*), Sidgwick and Springall (*loc. cit.*), and Baker (this vol., p. 476) has confirmed

structure (IV) for hydrindene derivatives. Our results also are in agreement with this formula, as a double bond is shown to exist between C_5 and C_6 and a single bond between C_4 and C_5 . The stabilised form for tetralin (V) may hold for the hydrocarbon as advocated by Mills and Nixon, but it apparently does not hold for all its derivatives. Thus, while the bromination and coupling reactions of 6-hydroxytetralin point to structure (V) (cf. Mills and Nixon, *loc. cit.*), the Skraup reaction on 6-aminotetralin (v. Braun and Gruber, *Ber.*, 1922, 55, 1710) indicates a preponderance of form (VI). The fact that in all the reactions mixtures were obtained, and the work of Fieser and Lothrop (*loc. cit.*) and Sidgwick and Springall (*loc. cit.*) provides evidence that the bonds in tetralin derivatives are not fixed. Our observation that 6-bromo-5-nitrotetralin is completely non-reactive and 7-bromo-6-nitrotetralin reactive indicates structure (VI). It may be that the presence of the bromo- and the nitro-group does stabilise the molecule in this way, or it is possible that the reduced ring has some inhibiting effect on the bromine reactivity (cf. Lindemann and Pabst, *Annalen*, 1928, 462, 24). It is impossible at present to decide between these alternatives.

Borsche and Bodenstein (*Ber.*, 1926, 59, 1909) claimed to have obtained 6-bromo-5-acetamidohydrindene and 4-nitro-5-acetamidohydrindene by the bromination and nitration respectively of 5-acetamidohydrindene. From these two compounds we obtained the corresponding bromonitrohydrindenenes by hydrolysis to the amino-compounds and replacement of the amino-group by the nitro-group in 6-bromo-5-aminohydrindene and by the bromo-group in the nitroaminohydrindene. The two bromonitrohydrindenenes so obtained were found to be identical by a mixed melting-point determination and by measurements of the bromine reactivity. The nitro-compound obtained by Borsche and Bodenstein must therefore have been the 6-nitro- and not the 4-nitro-compound. It also follows that their product of the nitration of 5-acetylhydrindene must have been 6-nitro-5-acetylhydrindene and not 4-nitro-5-acetylhydrindene as they claimed. Doubt on some of the results of Borsche and Bodenstein had been cast by Lindner and Bruhin (*Ber.*, 1927, 60, 439).

In one case, 4-bromo-5-nitrohydrindene, we were unable to purify the compound thoroughly, but quantitative analysis showed it to be sufficiently pure for a rough estimation of the bromine reactivity to be made.

EXPERIMENTAL.

Unless otherwise stated, the methods of preparation and the properties of the compounds used are those given in the literature. Many of the bromonitro-compounds were prepared from the corresponding nitroamines, the method of Hodgson and Walker (J., 1933, 1620) always being used. The identity and purity of the nitroamino-compounds were checked by the preparation of acetyl or benzoyl derivatives or of molecular compounds with *s*-trinitrobenzene. The bromonitro-compounds in most instances were analysed quantitatively (Dr. Weiler, Oxford).

3-Bromo-2-nitronaphthalene.—1 : 3-Dibromo- β -naphthylamine was prepared as described by Bell (*loc. cit.*) and from it 3-bromo- β -naphthylamine was obtained as described by Consden and Kenyon (J., 1935, 1591). Attempts to oxidise the amino-group to the nitro-group by the methods of Meisenheimer and Hesse (*Ber.*, 1919, 52, 1172) and Bigiavi and Albanese (*Centr.*, 1935, 1348) were unsuccessful. The compound was therefore converted into the nitro-compound by the method of Hantzsch and Blagden (*Ber.*, 1900, 33, 2554). Copper sulphate crystals (10 g.) were dissolved in water (100 c.c.), and 2*N*-sodium hydroxide added until all the copper was precipitated as the hydroxide. The mixture was cooled in ice, and sulphur dioxide passed in until a dark green solution was obtained. When this was warmed, a red precipitate of cupro-cupri-sulphite (5 g.) was obtained. The amine (6 g.) was converted into the sulphate by the addition of sulphuric acid, water (25 c.c.) added to the paste, and the amine diazotised. A mixture of cupro-cupri-sulphite (10 g.), sodium nitrite (32 g.), and water (120 c.c.) was stirred mechanically, and the diazo-solution added drop by drop. The mixture was stirred at room temperature until the brisk evolution of gas had ceased, and then distilled with superheated steam. This method of separation was tedious owing to the low volatility of the 3-bromo-2-nitronaphthalene. The product (0.5 g.) crystallised from alcohol in pale yellow needles, m. p. 84° (Found: N, 5.7; Br, 33.4. Calc. for $C_{10}H_6O_2NBr$: N, 5.6; Br, 31.7%). Hodgson (J., 1936, 1151) gives the same m. p.

5-Bromo-1-nitronaphthalene.—This compound was prepared by a modification of Scheufelin's method (*Annalen*, 1885, 231, 185). A mixture of α -nitronaphthalene (20 g.) and ferric chloride

(0.5 g.) was liquefied on a water-bath, and bromine passed through it for 1 hour, hydrogen bromide being evolved. The product was poured into water, washed with sodium carbonate solution, and crystallised repeatedly from alcohol (charcoal), 4 g. of yellow needles, m. p. 121° (lit., 122.5°), being obtained (Found: N, 5.3; Br, 31.5. Calc. for $C_{10}H_6O_2NBr$: N, 5.6; Br, 31.7%).

6-Bromo-2-nitronaphthalene.—6-Bromo- β -naphthylamine, prepared by the method of Saunders and Hamilton (*J. Amer. Chem. Soc.*, 1932, 54, 636), crystallised from glacial acetic acid in yellow plates, m. p. 206—207° (lit., 203°). After diazotisation it yielded 6-bromo-2-nitronaphthalene, which crystallised from glacial acetic acid in brown-yellow needles, m. p. 190° (Found: N, 5.6; Br, 31.3. $C_{10}H_6O_2NBr$ requires N, 5.6; Br, 31.7%).

5 : 8-Dibromo-1-nitronaphthalene.—This compound was prepared by a modification of Salkind's method (*Ber.*, 1931, 64, 958), 1 : 4-dibromonaphthalene (19 g.) and concentrated nitric acid (110 c.c.) being stirred together at 65° for 4 hours. The precipitate obtained on cooling was crystallised repeatedly from glacial acetic acid, yielding 6.5 g. of pale yellow needles, m. p. 118° (lit., 116—117°).

4 : 6-Dibromo-5-p-toluenesulphonamidohydrindene.—6-Bromo-5-aminohydrindene (Borsche and Bodenstein, *loc. cit.*) (18 g.) was dissolved in pyridine (50 c.c.), and *p*-toluenesulphonyl chloride (16.5 g.) added. The solution was boiled for 20 minutes and cooled, bromine (4.5 c.c.) added slowly, and the mixture kept overnight and poured into water. The sticky mass obtained solidified on trituration with cold alcohol (100 c.c.). **4 : 6-Dibromo-5-p-toluenesulphonamidohydrindene** (12 g.) crystallised from alcohol in colourless prisms, m. p. 199—200° (Found: Br, 36.7; S, 7.2. $C_{18}H_{15}O_2NBr_2S$ requires Br, 35.9; S, 7.2%).

4 : 6-Dibromo-5-aminohydrindene.—The preceding compound (11 g.) was dissolved in warm concentrated sulphuric acid (120 c.c.), and the solution poured into a large volume of water, 4 : 6-dibromo-5-aminohydrindene separating. It crystallised from alcohol in colourless needles, m. p. 71° (Borsche and Bodenstein, *loc. cit.*, record 70°) (Found: Br, 53.8. Calc. for $C_9H_5NBr_2$: Br, 54.9%).

4-Bromo-5-aminohydrindene.—4 : 6-Dibromo-5-aminohydrindene (8 g.) was heated for 1 hour with alcohol (40 c.c.), concentrated hydrochloric acid (40 c.c.), and tin (8 g.). After 40 minutes the solution was filtered hot and poured into 2*N*-sodium hydroxide (250 c.c.), and the dark grey compound extracted with alcohol. Water was added to the alcoholic solution until it became milky; after 12 hours, long white needles (2 g.) of 4-bromo-5-aminohydrindene separated, m. p. 50—51° (Found: N, 6.4; Br, 39.5. C_9H_7ONBr requires N, 6.6; Br, 37.6%). An oil was obtained by mixing the compound with 6-bromo-5-aminohydrindene, showing that the reduction had removed the 6-bromine atom.

4-Bromo-5-nitrohydrindene.—4-Bromo-5-aminohydrindene was converted into 4-bromo-5-nitrohydrindene by the method used for preparing 3-bromo-2-nitronaphthalene (see above). The reaction mixture on steam distillation gave a pale yellow oil, but attempts to crystallise it met with no success. As in all cases of preparations of nitro-compounds by this method, the yield was exceedingly small, and we had little more than was sufficient for reactivity measurements and analysis (Found: N, 4.3; Br, 35.2. $C_9H_6O_2NBr$ requires N, 6.0; Br, 33.0%).

6-Bromo-5-nitrohydrindene.—6-Bromo-5-aminohydrindene (3.5 g.), m. p. 46—47° (Borsche and Bodenstein, *loc. cit.*, record 43°), was converted into 6-bromo-5-nitrohydrindene by the method just mentioned. The reaction mixture was steam-distilled for 6 hours, and an oil obtained which was dissolved in ether-methyl alcohol. When the ether was allowed to evaporate at room temperature, the solution deposited 6-bromo-5-nitrohydrindene in yellow needles (0.5 g.), m. p. 42°. The compound was also prepared by standard methods from the nitro-5-acetamidohydrindene of Borsche and Bodenstein (*loc. cit.*) and purified by dissolving it in methyl alcohol and cooling the solution in a freezing mixture; m. p. 44—45°. The compound was shown to be identical with 6-bromo-5-nitrohydrindene by mixed m. p. determination and bromine reactivity (Found: N, 6.0; Br, 32.8. $C_9H_6O_2NBr$ requires N, 6.0; Br, 33.0%).

6-Bromo-7-nitrotetralin.—6-Acetyltetralin was converted into 6-acetamidotetralin by Scharwin's method (*Ber.*, 1902, 35, 2513), but, as phosphorus pentachloride was found to be unsatisfactory for the Beckmann rearrangement involved, benzenesulphonyl chloride (cf. Blatt and Barnes, *J. Amer. Chem. Soc.*, 1934, 56, 1150) was used. The oxime of 6-acetyltetralin (10 g.) was dissolved in pyridine (100 c.c.), and benzenesulphonyl chloride (12 c.c.) slowly added, the temperature being kept below 15°. After 3 hours the solution was poured into ice and dilute hydrochloric acid. After several hours 6-acetamidotetralin separated and was crystallised from ligroin, m. p. 107°; yield, 6 g. If larger quantities of oxime were used, charring occurred and the yield diminished. The compound was nitrated (Schroeter, *Annalen*, 1921, 426, 66), and

from the resulting 7-nitro-6-acetoamidotetralin 6-bromo-7-nitrotetralin was prepared by standard methods; it formed prisms from methyl alcohol, m. p. 53—54° (Found: N, 5.3; Br, 31.3, $C_{10}H_9O_2NBr$ requires N, 5.5; Br, 31.3%).

6-Bromo-5-nitrotetralin.—Prepared by the usual methods from 5-nitro-6-acetoamidotetralin (Schroeter, *loc. cit.*), this formed golden-yellow plates from alcohol, m. p. 103—104° (Vesely and Chudozilow, *Chem. Abs.*, 1925, 128, 1056, record 101—102°) (Found: N, 5.7; Br, 30.6. Calc. for $C_{10}H_9O_2NBr$: N, 5.5; Br, 31.3%).

Quantitative Method.—The method followed was that of Salkind (*Ber.*, 1931, 64, 289), as it was found to be suitable for small quantities of material. About 0.1 g. of the bromo(chloro)-compound was accurately weighed in a glass tube provided with a ground glass stopper. Piperidine (1 c.c.) was added, and the tube immersed in a thermostat at approximately 45°. After a definite interval of time the contents of the tube were washed into a separating funnel with water (50 c.c.), and the solution shaken with pure benzene, which removed coloured organic matter from the aqueous layer but no halogen. The aqueous layer was now almost colourless. The halogen present was determined by Volhard's method by titration with silver nitrate (*N*/50) and potassium thiocyanate (*N*/50), ferric alum being used as indicator. All determinations were done in duplicate.

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THE STRUCTURE OF AROMATIC COMPOUNDS. PART II.

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96. *The Structure of Aromatic Compounds. Part II.*

By NEIL CAMPBELL, W. ANDERSON, and J. GILMORE.

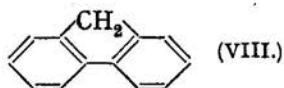
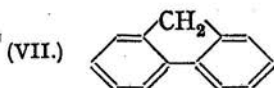
The results of a previous paper on the structure of aromatic hydrocarbons (Part I, McLeish and Campbell, J., 1937, 1103) have been revised in terms of the resonance theory. The halogen reactivity of halogenonitro-compounds of styrene, phenanthrene, diphenyl, hydrindene, fluorene, and acenaphthene has been measured, and the results correlated with the fine structure of the compounds.

THE problem of the structure of the aromatic polycyclic hydrocarbons has recently been revised in terms of the theory of resonance (for summary, see Taylor and Brockway, *Ann. Reports*, 1937, 196). Naphthalene may accordingly be represented by (I) as the resultant of the three unexcited structures, the heavy lines indicating those bonds with greater

The non-reactivity of 2-bromo-4', 4-bromo-4', and 4-bromo-2'-nitrodiphenyl, and of 2-bromo-7-nitrofluorene shows that the influence of the nitro-groups is not transmitted from one ring to the other. This supports the conclusion of Le Fèvre and Turner (J., 1928, 246) on the independence of the two nuclei in the diphenyl molecule.

Previous measurements of the reactivity of 4-bromo-5-nitrohydrindene (McLeish and Campbell, *loc. cit.*) were not satisfactory, as the compound was not pure. We have repeated the preparation, and obtained on fractional distillation an oil which, when immersed in carbon dioxide-ether, yielded a crystalline compound, m. p. about 20°. The compound was found to be slightly reactive, thus confirming our previous result.

The reactivities of some bromonitroacenaphthenes and fluorenes were measured, but the results are not conclusive, as all the required compounds were not obtained. The pronounced reactivity of 3-bromo-2-nitroacenaphthene suggests that acenaphthene contains a nucleus similar to that of naphthalene (I). This is to be expected, for acenaphthene has the same resonance energy as naphthalene (Pauling and Sherman, *J. Chem. Physics*, 1933, 1, 606). The reactivities of the fluorene compounds and the substitution reactions of compounds such as 2-aminofluorene point to the structure (VII), but the similarity of fluorene to indene and cyclopentadiene (Thiele and Henle, *Annalen*, 1906, 347, 290) supports structure (VIII). It is therefore reasonable to conclude that fluorene is a resonance hybrid of forms such as (VII) and (VIII), and Lothrop's results (*J. Amer. Chem. Soc.*, 1939, 61, 2115) from a study of 2-hydroxyfluorene can be explained in this way. The results of Pauling and Sherman (*loc. cit.*) show that fluorene is indeed a resonance hybrid, the main contributing forms being the Kekulé structures.



Most efforts to prepare fluorene derivatives substituted in position 1 have been unsuccessful (*e.g.*, Eckert and Langecker, *J. pr. Chem.*, 1928, 118, 277). An attempt was made to prepare 1:2-substituted derivatives by the method used to prepare 2-bromo-3-aminonaphthalene (Part I, *loc. cit.*). Bromination of 2-*p*-toluenesulphonamidofluorene yielded, however, the 3:7-dibromo-compound. Similarly, bromination of 2-acetamidofluorene yielded 3:7-dibromo-2-acetamidofluorene.

The presence of a methyl group was shown to decrease the halogen reactivity in the bromonitrotoluenes. This influence has already been noted (*e.g.*, Kenner, J., 1914, 105, 2717), but no adequate explanation has yet been given (*cf.* Lindemann and Pabst, *Annalen*, 1928, 462, 24).

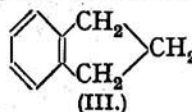
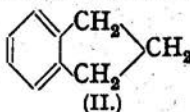
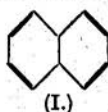
2-*p*-Toluenesulphonamidotoluene was brominated in the hope that the bromine would substitute in the 3-position, and from this compound 3-bromo-2-nitrotoluene could be prepared. Bromination, however, was shown to occur in position 5.

EXPERIMENTAL.

Unless otherwise stated, the methods of preparation and the properties of the compounds used are those given in the literature. Hodgson and Walker's diazotisation method (J., 1933, 1620) was used, and the amino-group was converted into the nitro-group by the method of Hantzsch and Blagden (*Ber.*, 1900, 33, 2554). The purity of all compounds was checked by the sharpness of their m. p.'s on the Kofler micro-apparatus (*Mikrochem.*, 1934, 15, 242). Sublimations were effected on this apparatus. All analyses were done by Mr. Brown, Edinburgh.

Halogeno- ω -nitrostyrenes.—Various methods were investigated for the condensation of nitromethane and aromatic aldehydes. The use of zinc chloride (Posner, *Ber.*, 1898, 31, 656) was very unsatisfactory. Amines (Knoevenagel and Walter, *loc. cit.*) yielded better results, and it is noteworthy that, although neither *n*-butylamine nor piperidine gave appreciable yields, yet a mixture of the two was an effective condensing agent. The most satisfactory results were obtained with alcoholic potassium hydroxide (Thiele, *Ber.*, 1899, 32, 1293; Remfrey, J., 1911, 99, 282), the modification of Thiele and Haeckel (*Annalen*, 1902, 325, 7) being finally adopted.

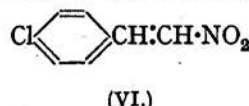
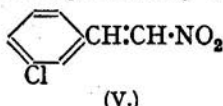
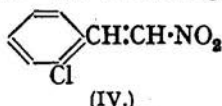
double-bond character. Hydrindene has forms (II) and (III) as the main contributing structures, and its chemical properties may be accounted for by the slight predominance of (II) (Sutton and Pauling, *Trans. Faraday Soc.*, 1935, **31**, 939). It is therefore necessary to abandon the theory of fixed structures, and to conclude that polycyclic aromatic compounds



are resonance hybrids, the chemical properties of which are explained by the non-equivalence of the carbon-carbon linkages. This accounts for the reactivity of 2-bromo-1-nitro- in contrast to the non-reactivity of 2-bromo-3-nitro-naphthalene; for the much greater reactivity of 5-bromo-6-nitro- than of 4-bromo-5-nitro-hydrindene (Part I, *loc. cit.*), and for the findings of Lindner, Sellner, Hofmann, and Hager (*Monatsh.*, 1939, **72**, 335) and of Evans and Sandin (*J. Amer. Chem. Soc.*, 1939, **61**, 2916).

In the present research the method used to determine the fine structure of aromatic compounds (Part I, *loc. cit.*) has been applied to certain other compounds, and the effect of methyl groups on the bromine reactivity of bromonitro-compounds has been studied. The reactivities were measured as before by the piperidine method, and the results are given in the table.

The reactivity of 9-bromo-10-nitrophenanthrene and the non-reactivity of 3-bromo-4-nitroacenaphthene supply evidence for the essential correctness of Fuson's vinylogy theory (*Chem. Reviews*, 1935, **16**, 1). The former contains the $\text{Br}-\text{C}=\text{C}-\text{NO}_2$ fragment in which the carbon-carbon linkage has 4/5 double-bond character, and in the latter compound the bromo- and the nitro-group, although in many respects *ortho* to one another, are not



separated by the bond system necessary for reactivity. Further support for Fuson's theory is obtained from the reactivities of *o*-bromo- ω -nitrostyrene and the three isomeric chloro- ω -nitrostyrenes (IV), (V), and (VI). As was anticipated, only the *m*-compound was non-reactive. The results of the hydrolysis of the ω -bromonitrostyrenes (Dann, Howard, and Davies, *J.*, 1928, 605) also support the theory.

It was of interest to measure the reactivities of 2-bromo- and 4-bromo- α -nitrostilbene, but attempts to obtain these compounds by condensing phenylnitromethane with the necessary aldehyde by the method of Knoevenagel and Walter (*Ber.*, 1904, **37**, 4502) yielded either 3 : 5-diphenyl-4-bromophenyl- or 3 : 4-diphenyl-5-bromophenyl-isooxazoles depending on the mechanism of formation (Heim, *Ber.*, 1911, **44**, 2016; Kohler and Barrett, *J. Amer. Chem. Soc.*, 1924, **46**, 2106; Worrall, *ibid.*, 1935, **57**, 2299; Ruggli and Hegedüs, *Helv. Chim. Acta*, 1939, **22**, 405).

	Removal of bromine, %.			Removal of bromine, %.	
	1 Hr.	24 Hrs.		1 Hr.	24 Hrs.
9-Bromophenanthrene	0	0	2-Bromo-3-nitrofluorene	50	97
9-Bromo-10-nitrophenanthrene	69	100	3-Bromoacenaphthene	—	0
<i>o</i> -Bromo- ω -nitrostyrene	—	34	3-Bromo-2-nitroacenaphthene ...	68	100
<i>o</i> -Chloro- ω -nitrostyrene	—	13 *	3-Bromo-4-nitroacenaphthene ..	—	0
<i>m</i> -Chloro- ω -nitrostyrene	—	0 *	4-Bromo-1-nitroacenaphthene ...	—	2
<i>p</i> -Chloro- ω -nitrostyrene	—	8 *	<i>o</i> -Bromonitrobenzene	53	96
4-Bromodiphenyl	—	0	<i>m</i> -Bromonitrobenzene	—	0
2-Bromo-4'-nitrodiphenyl	—	0	<i>p</i> -Bromonitrobenzene	96	104
4-Bromo-4'-nitrodiphenyl	—	0	2-Bromo-3-nitrotoluene	1	4
4-Bromo-3-nitrodiphenyl	78	98	4-Bromo-3-nitrotoluene	13	91
4-Bromo-2'-nitrodiphenyl	—	0	2-Bromo-4-nitrotoluene	0	0
3-Bromo-4'-nitrodiphenyl	—	0	2-Bromo-5-nitrotoluene	—	8
4-Bromo-5-nitrohydrindene ...	—	7	5-Bromo-2-nitrotoluene	0	51
2-Bromo-5-nitrohydrindene ...	—	0	3-Bromo-4-nitrotoluene	54	99
2-Bromo-7-nitrofluorene	—	0			

* 48 Hours.

(0.4 g.) in chloroform (10 c.c.) added. The solution was heated on the water-bath for 1 hour and the chloroform removed by distillation. The residual oil on trituration with alcohol yielded a solid which crystallised from carbitol in needles, m. p. 203°, identical (mixed m. p.) with the dibromosulphonamido-compound, m. p. 203°, prepared below.

2-Aminofluorene (5 g.) and *p*-toluenesulphonyl chloride (6 g.) in pyridine were heated for 1 hour under reflux. *2-p-Toluenesulphonamidofluorene* was isolated in the usual way, and crystallised from glacial acetic acid or carbitol in colourless prisms (7 g.), m. p. 157—158° (Found: N, 4.4. $C_{20}H_{17}O_2NS$ requires N, 4.4%). This compound (7 g., 1 mol.) was dissolved in chloroform, bromine (6.7 g., 2 mols.) added, and the mixture heated on the water-bath for $\frac{1}{2}$ hour. The chloroform was removed by distillation, and the resulting **3:7-dibromo-2-p-toluenesulphonamidofluorene** crystallised several times from alcohol; m. p. 203°; yield, 8.7 g. (Found: N, 2.8; Br, 31.3. $C_{20}H_{15}O_2NBr_2S$ requires N, 2.8; Br, 32.4%). The compound was hydrolysed by dissolving it in concentrated sulphuric acid at 40° and pouring it into water. The white flocculent precipitate obtained was triturated with 30% sodium hydroxide. **3:7-Dibromo-2-aminofluorene** crystallised from alcohol in prisms, m. p. 135°; yield, almost theoretical (Found: N, 4.1; Br, 48.7. $C_{18}H_9NBr_2$ requires N, 4.1; Br, 47.2%).

3:7-Dibromofluorene.—**3:7-Dibromo-2-aminofluorene** (2 g.) was diazotised, the solution diluted with an equal volume of alcohol, warmed to 80°, and poured into water when the evolution of gas had ceased. The precipitated **3:7-dibromofluorene** was recrystallised from methyl alcohol; m. p. 129°; yield, 0.5 g. (Found: Br, 48.1. $C_{18}H_8Br_2$ requires Br, 49.4%). Further purification by repeated sublimation yielded prisms or needles, m. p. 133°.

3:7-Dibromofluorenone.—**3:7-Dibromofluorene** (0.2 g.) was boiled under reflux for 3 hours with sodium dichromate (1 g.) and acetic acid (2 c.c.). The mixture was cooled, diluted with water, and the yellow precipitate crystallised from glacial acetic acid; m. p. 200°; yield, 80% (Found: Br, 47.5. $C_{18}H_6OBr_2$ requires Br, 47.3%).

Bromination of 2-Bromo-7-acetamidofluorene.—**2-Bromo-7-aminofluorene** (1 g.) was dissolved in boiling tetralin and acetic anhydride (2 c.c.) added. A solid separated immediately, and was purified by sublimation or by crystallisation from carbitol, forming prisms, m. p. 229—231° (Found: N, 5.0. $C_{18}H_{12}ONBr$ requires N, 4.6%). The *acetyl* compound was suspended in chloroform (20 c.c.), and bromine (0.3 g.) in chloroform (5 c.c.) added. Pyridine was then added until a clear solution was obtained, and this was kept at room temperature for 1 hour. The chloroform was removed by distillation, and the residue on treatment with dilute hydrochloric acid yielded a solid, which crystallised from carbitol in prisms, m. p. 263—265° (Found: Br, 41.0. $C_{18}H_{11}ONBr_2$ requires Br, 42.0%). The compound was identical with **3:7-dibromo-2-acetamidofluorene** obtained by acetylation of **3:7-dibromo-2-aminofluorene** in tetralin by acetic anhydride; it was further purified by sublimation, elongated prisms or needles, m. p. 272°, being obtained.

3-Bromo-4-nitroacenaphthene.—This compound was obtained by Dziewonski, Schoen, and Glazner (*Chem. Abstracts*, 1931, 25, 1518) but no experimental details are available. **3-Bromo-4-nitroacenaphthene** (8 g.) was dissolved in hot glacial acetic acid (40 c.c.), the solution quickly cooled to 10°, and vigorously stirred while concentrated nitric acid (5 c.c.) was slowly run in. **3-Bromo-4-nitroacenaphthene** separated; it crystallised from alcohol in light yellow prisms, m. p. 155° (lit., 159—161°); yield, 65%.

4(?) -Bromo-1-nitroacenaphthene.—**1-Nitroacenaphthene** (5 g.) was dissolved in glacial acetic acid (25 c.c.), bromine (4 g.) added, and the solution heated to boiling; on cooling, it deposited **4-bromo-1-nitroacenaphthene**, which was crystallised several times from alcohol; m. p. 157°; yield, 2 g. (Found: N, 5.3; Br, 28.7. $C_{12}H_8O_2NBr$ requires N, 5.0; Br, 28.7%). It sublimes in elongated prisms. By analogy with the bromination of the nitronaphthalenes, the bromine is believed to be in the 4-position.

3-Bromo-2-nitroacenaphthene.—This compound was prepared by the diazotisation of **2-nitro-3-aminoacenaphthene**, and was crystallised first from alcohol and then from light petroleum (b. p. 80—100°), forming golden prisms, m. p. 143°; yield, 66% (Found: Br, 29.1%).

3-Bromo-4-nitrotoluene.—Prepared by the diazotisation of **3-bromo-4-aminotoluene** (6 g.), this compound was purified by steam-distillation, followed by crystallisation from methyl alcohol; it formed pale yellow needles (2 g.), m. p. 36—37° (Found: Br, 36.7. Calc. for $C_7H_6O_2NBr$: Br, 37.0%).

Bromination of 2-p-Toluenesulphonamidotoluene.—*o*-Toluidine (15 g.) and *p*-toluenesulphonyl chloride (27 g.) were dissolved in pyridine (140 c.c.), bromine (7.1 c.c.) added, and the solution kept overnight. The product, isolated by the usual procedure, crystallised from alcohol in prisms, m. p. 136°; yield, theoretical. The **5-bromo-p-toluenesulphonamidotoluene** was identical

o-Chloro- ω -nitrostyrene was prepared by cooling *o*-chlorobenzaldehyde (3 g.) and nitromethane (2.2 g.) in a freezing mixture, and carefully adding sodium hydroxide (1.5 g.) in water (3 c.c.). After an induction period, a bulky white precipitate separated, and methyl alcohol was added if the mixture became too thick to stir. The reaction was complete when a sample gave a clear solution with water. Addition of concentrated hydrochloric acid (20 c.c.) and water (10 c.c.) yielded yellow crystals which, after being washed with water, were crystallised from alcohol; m. p. 47° (Found: Cl, 19.6. $C_8H_6O_2NCl$ requires Cl, 19.1%). By similar methods were obtained the *m*-chloro- and the *p*-chloro-compounds, yellow crystals, m. p. 48–49° (Found: Cl, 20.0%), and elongated yellow prisms, m. p. 113–114° (Found: N, 7.0; Cl, 18.4. $C_8H_6O_2NCl$ requires N, 6.1; Cl, 19.1%), respectively. The yields in all cases were good.

o-Bromobenzaldehyde was prepared by a method similar to that of Brady and Lahiri (J., 1934, 1956). The 2:4-dinitrophenylhydrazones separated from tetralin in orange needles, m. p. 199–200° (Found: N, 15.3. $C_{13}H_9O_4N_2Br$ requires N, 15.3%). *o*-Bromo- ω -nitrostyrene was obtained in 50% yield by keeping *o*-bromobenzaldehyde (1 g.) and nitromethane (0.33 g.) for 3 days with one drop each of piperidine and *n*-butylamine; yellow crystals (alcohol), m. p. 86° (Found: Br, 34.2. $C_8H_6O_2NBr$ requires Br, 34.7%).

Condensation of o- and p-Bromobenzaldehydes and Phenylnitromethane.—*o*-Bromobenzaldehyde (1 g.), phenylnitromethane (0.74 g.), methylamine hydrochloride (0.1 g.), sodium carbonate (0.04 g.), and a few drops of ethyl alcohol were heated under reflux for 24 hours. Crystals separated, which were crystallised several times from ligroin; m. p. 135°, yield 0.5 g. The compound was a diphenyl-*o*-bromophenylisooxazole (Found: C, 67.4; H, 4.2; N, 3.8; Br, 20.1. $C_{21}H_{14}ONBr$ requires C, 67.0; H, 3.7; N, 3.7; Br, 21.3%). *p*-Bromobenzaldehyde similarly yielded 0.5 g. of an isomer, m. p. 175° (Found: N, 3.9; Br, 19.6%), which sublimed in needles and then had m. p. 180°.

4-Nitrodiphenyl.—The method of Fichter and Sulzberger (*Ber.*, 1904, 37, 881) required modification. 4-Acetamidodiphenyl was prepared by suspending 4-aminodiphenyl (200 g.) in benzene (200 c.c.) and adding acetic anhydride (120 g.) carefully, the mixture being cooled with running water. After 15 minutes the acetamido-compound was separated, well washed with water, and when thoroughly dry was sufficiently pure for the next stage. 4-Acetamidodiphenyl (180 g.) was dissolved in glacial acetic acid and the solution warmed to 70° on the water-bath. Fuming nitric acid (200 g., *d* 1.51) mixed with an equal volume of glacial acetic acid was gradually added, with good stirring. The mixture was kept at 70° for 1 hour, and then poured into twice its volume of cold water. 3-Nitro-4-acetamidodiphenyl separated, and crystallised from alcohol in yellow needles (200 g.), m. p. 132° (lit., 132°). The compound was suspended in boiling alcohol (1 l.), and potassium hydroxide (100 g.) in water (125 c.c.) added. A mass of dark red crystals separated after a few minutes, and was purified by washing with 30% aqueous alcohol. Yield, 166 g., m. p. 167–169° (lit., 169°). 3-Nitro-4-aminodiphenyl (160 g.) was added to a mixture of 95% alcohol (390 c.c.) and concentrated sulphuric acid (58 c.c.), and the mixture heated until a clear solution was obtained. The mixture, cooled and vigorously stirred, was diazotised in the usual manner, and kept at room temperature for 3 hours. Copper bronze (6 g.) was then added in portions, the mixture being kept in cold water. The temperature rose to 40°, and nitrogen and acetaldehyde were copiously evolved. The alcohol was removed by distillation, and the residue distilled in a current of superheated steam, the flask being immersed in an oil-bath maintained at 210°. The 4-nitrodiphenyl crystallised from alcohol in yellow needles (60 g.), m. p. 62° (lit., 62°).

4-Bromo-3-nitrodiphenyl.—Prepared from 3-nitro-4-aminodiphenyl (6.5 g.) by diazotisation, this compound crystallised from light petroleum (b. p. 40–60°) in long yellow prisms (4.5 g.), m. p. 41–42° (Found: N, 4.9; Br, 27.6. $C_{12}H_8O_2NBr$ requires N, 5.0; Br, 28.7%).

5-Bromo-2-nitrodiphenyl.—The amino-group of 5-bromo-2-aminodiphenyl was converted into the nitro-group, and the resulting compound crystallised from ligroin in light brown needles, m. p. 230°; yield 2%. This compound is believed to be 5-bromo-2-nitrodiphenyl, but its m. p. is abnormally high (Found: N, 5.3; Br, 28.9%).

2-Bromo-3-nitrofluorene.—Prepared by diazotisation of 3-nitro-2-aminofluorene, this compound formed dark red needles from glacial acetic acid, m. p. 120–121° (Found: N, 5.0; Br, 28.4. $C_{15}H_9O_2NBr$ requires N, 4.8; Br, 27.6%).

3:7-Dibromo-2-aminofluorene.—Equimolecular quantities of 2-bromo-7-aminofluorene and *p*-toluenesulphonyl chloride in pyridine were mixed, kept overnight, and poured into dilute hydrochloric acid. The resulting 2-bromo-7-*p*-toluenesulphonamidofluorene was obtained as elongated prisms (isopropyl alcohol or carbitol), m. p. 211° (Found: N, 3.8. $C_{20}H_{16}O_2NBrS$ requires N, 3.4%). This compound (1 g.) was dissolved in chloroform (50 c.c.), and bromine

with that prepared by the interaction of *p*-toluenesulphonyl chloride with 5-bromo-*o*-toluidine (Found: Br, 23.2. $C_{11}H_{11}O_2NBrS$ requires Br, 23.5%).

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**THE STRUCTURE OF AROMATIC COMPOUNDS.
PART III. THE ACTION OF ACETYL CHLORIDE
ON α - AND β -NAPHTHYLMETHYLMAGNESIUM
HALIDES**

BY
**NEIL CAMPBELL,
W. ANDERSON,
AND
J. GILMORE**

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154. *The Structure of Aromatic Compounds. Part III. The Action of Acetyl Chloride on α - and β -Naphthylmethylmagnesium Halides.*

By NEIL CAMPBELL, W. ANDERSON, and J. GILMORE.

α -Naphthylmethylmagnesium chloride reacts with acetyl chloride to give 1 : 3-di- α -naphthyl-2-methylpropylene, the structure of which was established by ozonolysis. The isomeric hydrocarbon derived from β -naphthylmethylmagnesium chloride probably has an analogous structure.

CERTAIN reagents with benzylmagnesium chloride and cinnamyl chloride give unexpected products due to molecular rearrangement (Tiffeneau and Delange, *Compt. rend.*, 1903, **137**, 573; Gilman and Harris, *J. Amer. Chem. Soc.*, 1927, **49**, 1825; Gilman and Kirkby, *ibid.*, 1932, **54**, 345; Austin and Johnston, *ibid.*, p. 647; Coleman and Forrester, *ibid.*, 1936, **58**, 27; Young, Ballou, and Nozaki, *ibid.*, 1939, **61**, 12). Compounds containing the fragment $C:C\cdot CH_2\cdot MgCl$ may therefore be expected under certain conditions to undergo rearrangement. The observation that α -naphthylmethylmagnesium chloride gives "abnormal" products accordingly affords evidence that the $\alpha\beta$ -linkage possesses decided double-bond

boiled for $\frac{1}{2}$ hour, and after being cooled in carbon dioxide-ether was filtered through glass wool into a cooled solution of acetyl chloride (5 g.) in ether. The white precipitate which immediately formed was decomposed with ice-cold dilute hydrochloric acid, and the solution extracted with ether, which on evaporation yielded 1 : 3-di- β -naphthyl-2-methylpropylene (4.5 g.), m. p. 184–185° after recrystallisation from glacial acetic acid (Found : C, 93.6; H, 6.5. $C_{24}H_{20}$ requires C, 93.5; H, 6.5%). It did not decolorise alkaline permanganate or bromine in carbon tetrachloride. Compounds containing a double bond, however, frequently do not react with these reagents, especially when one of the carbon atoms attached to the double bond holds no hydrogen (Gilman's "Organic Chemistry," vol. 1, p. 546).

α -Naphthylmethylmagnesium Chloride and Acetyl Chloride.— α -Naphthylmethyl chloride was prepared by the method of Coles and Dodds (*J. Amer. Chem. Soc.*, 1938, 60, 853; b. p. 164–167°/16 mm. (lit., 158–159°/14 mm.)). When the mixture of naphthalene, formaldehyde, and concentrated hydrochloric acid was kept at room temperature for 48 hours before the addition of sulphuric acid, a better yield was obtained and less unchanged naphthalene remained. The preparation of the Grignard reagent and the addition of acetyl chloride to it were carried out as described above, except that the mixture was finally heated under reflux for 4 hours. Evaporation of the ether yielded an oil, which was purified by dissolving it in light petroleum (b. p. 40–60°) and immersing the solution in carbon dioxide-ether. An impurity separated, and the clear solution was decanted and on evaporation gave a white solid, m. p. 162–163°, in very poor yield (Found : C, 93.4; H, 6.6. $C_{24}H_{20}$ requires C, 93.5; H, 6.5%). Ozonisation of the hydrocarbon in carbon tetrachloride solution gave α -naphthoic acid (m. p. and mixed m. p. with an authentic sample) and an oil which on the usual treatment with 2 : 4-dinitrophenylhydrazine gave a 2 : 4-dinitrophenylhydrazone which was shown to be identical with that of α -naphthylacetone (see below); m. p. 174–176° after purification by sublimation. No formaldehyde was detected. The hydrocarbon is therefore 1 : 3-di- α -naphthyl-2-methylpropylene.

α -Naphthylacetone-2 : 4-dinitrophenylhydrazone.—A mixture of α -naphthylacetic acid and barium acetate was intimately mixed and distilled. The oily solid formed readily yielded a 2 : 4-dinitrophenylhydrazone, which crystallised from tetralin in orange plates, m. p. 174–176° (Found : N, 15.1. $C_{19}H_{16}O_4N_4$ requires N, 15.4%).

Dibenzylmethylcarbinol.—Methyl iodide (29 g.) was converted into the Grignard reagent and cooled to –5°. Dibenzyl ketone (21 g.) in ether was then slowly added, and the product isolated in the usual manner. The oil (13 g.) obtained was dissolved in light petroleum (b. p. 40–60°), and the solution cooled in carbon dioxide-ether. Impurity separated and the clear solution was decanted. Evaporation yielded a solid. The process was repeated several times and *dibenzylmethylcarbinol* was finally obtained as a white crystalline mass (8 g.), m. p. 26–27° (Found : C, 84.9; H, 8.0. $C_{16}H_{18}O$ requires C, 85.0; H, 7.9%).

Dehydration of Dibenzylmethylcarbinol.—The carbinol (3 g.) was added to phthalic anhydride (5 g.) and heated to 160°, and phosphoric oxide (1 g.) added in small portions during 1 hour. The mixture was heated for a further $\frac{1}{2}$ hour, cooled, boiled with sodium hydroxide solution, and then extracted with ether. From the extract an oil was obtained which distilled at 180°/15 mm. (Sabatier and Murat, *loc. cit.*, record 304°/760 mm.) (Found : C, 92.3; H, 7.7. $C_{16}H_{16}$ requires C, 92.3; H, 7.7%).

The unsaturated compound (2 g.) was suspended in glacial acetic acid (30 c.c.), and chromic acid (4 g.) in water (8 c.c.) added. The mixture was gently heated for 1 minute, and the brisk reaction which ensued was moderated by cooling. After $\frac{1}{2}$ hour the mixture was distilled in steam, and the distillate extracted with ether. The ethereal solution was shaken with caustic soda and evaporated. The oil obtained yielded a 2 : 4-dinitrophenylhydrazone, m. p. 147–149°, identical with that obtained from benzyl methyl ketone (mixed m. p.). The hydrocarbon is therefore 1 : 3-diphenyl-2-methylpropylene.

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character. In continuation of the work on the fine structure of naphthalene (McLeish and Campbell, J., 1937, 1103) it was of interest to study the interaction of α - and β -naphthylmethylmagnesium halides with acetyl chloride.

We found that α -naphthylmethylmagnesium chloride reacts with acetyl chloride to give 1 : 3-di- α -naphthyl-2-methylpropylene, $C_{10}H_7 \cdot CH : CMe \cdot CH_2 \cdot C_{10}H_7$, the structure of which was established by ozonolysis, α -naphthoic acid and α -naphthylacetone being produced. The isomeric hydrocarbon derived from β -naphthylmethylmagnesium chloride probably has an analogous structure. These products are doubtless formed from intermediate carbinols. In neither case were ketonic compounds due to rearrangement detected.

Analogous results were obtained by the dehydration of dibenzylmethylcarbinol: the product was 1 : 3-diphenyl-2-methylpropylene, since oxidation with chromic acid gave benzyl methyl ketone. Sabatier and Murat (*Compt. rend.*, 1913, 156, 1430) studied the dehydration of dibenzylmethylcarbinol, but did not analyse the carbinol or the hydrocarbon and made no attempt to determine the structure of the latter.

EXPERIMENTAL.

M. p.'s were determined in Kofler's apparatus (*Mikrochem.*, 1934, 15, 242), and analyses were done by Dr. Weiler (Oxford) and Mr. W. Brown (Edinburgh).

Preliminary experiments showed that it is necessary to obtain pure β -naphthylmethyl halide in order to prepare the Grignard reagent. It was difficult to obtain a good yield of bromo-compound by the bromination of β -methyl-naphthalene (Schulze, *Ber.*, 1884, 17, 1527), and in most of the experiments β -naphthylmethyl chloride prepared from the carbinol was used.

β -Naphthylcarbinol.— β -Naphthaldehyde was prepared from β -naphthonitrile by Stephen's method (Robinson and Fulton, J., 1939, 200). In preparing the stannous chloride it was found advisable to use the method of Stephen (J., 1930, 2786) and recrystallise the product from glacial acetic acid, the crystalline form obtained dissolving readily in ether. The naphthaldehyde invariably contained a considerable quantity of unchanged nitrile. Reduction of the aldehyde with a palladium-barium sulphate catalyst yielded β -methyl-naphthalene (m. p. 36°; picrate, m. p. 118°). Reduction of the aldehyde (6.2 g.) in ethyl alcohol (50 c.c.) with Adams's platinum catalyst and ferric chloride as promoter (0.5 c.c. of 0.1M-ferric chloride) gave the carbinol, which formed colourless needles from light petroleum (b. p. 60–80°), m. p. 80° (lit., 80°); yield, 80%. When excess of the promoter was used, further reduction occurred.

Attempts were made to prepare the carbinol by other methods. The method of Byron West (*J. Amer. Chem. Soc.*, 1920, 42, 1662) gave only a 27% yield from β -naphthoamide. Ziegler's method (*Ber.*, 1921, 54, 737) was unsuccessful, although this worker obtained the corresponding carbinol from α -bromonaphthalene in good yield. A mixture of magnesium turnings (1 g.), dry ether (10 c.c.), and ethyl iodide (0.3 g.) was stirred and boiled, and β -iodonaphthalene (10 g.) in ether (40 c.c.) added. When the reaction had moderated, the solution was cooled in a freezing mixture, and formaldehyde, generated from trioxymethylene, led in. The black mass obtained was treated with water and extracted with ether, which on evaporation yielded a brown solid (4.5 g.). This after crystallisation from methyl alcohol (twice) was found to be $\beta\beta'$ -dinaphthyl, m. p. 185° (lit., 188°); picrate, m. p. 184° (lit., 184°).

β -Naphthylmethyl Chloride.— β -Naphthylcarbinol (12 g.) was dissolved in dry toluene (50 c.c.), thionyl chloride (25 c.c.) gradually added, and the mixture boiled under reflux for 3 hours. After removal of the toluene and the excess of thionyl chloride by distillation the residue was distilled in a vacuum, the fraction, b. p. 170°/20 mm., being collected; m. p. 47° (lit., 48°).

β -Naphthylmethyl Bromide.—The method of Schulze (*loc. cit.*) had to be modified. β -Methyl-naphthalene was brominated at 240–260° in a quartz flask exposed to radiation from a mercury vapour lamp. If no such radiation were used, a glassy black solid was obtained from which no β -naphthylmethyl bromide could be isolated. In a series of experiments the yield of the bromide never exceeded 22%, a large amount of the methyl-naphthalene being recovered. The compound was best purified by distillation in a vacuum (b. p. 214°/100 mm.) and subsequent crystallisation from ethyl alcohol; m. p. 54° (lit., 56°).

β -Naphthylmethylmagnesium Halide and Acetyl Chloride.—The formation of the Grignard reagent was extremely capricious, and occurred in only three cases (one of the bromide and two of the chloride). β -Naphthylmethyl bromide (9 g.) in dry ether (40 c.c.) was added to a mixture of magnesium turnings (1 g.) in ether (40 c.c.). Two drops of ethyl iodide were added to start the reaction, which became vigorous and was moderated by cooling. The mixture was then

308. Studies in Qualitative Organic Analysis. Part II. Identification of Alkyl Halides, Aromatic Nitroso-compounds, Aromatic Hydrocarbons, and cyclopentadiene Compounds.

By (Miss) WINIFRED J. LEVY and NEIL CAMPBELL.

Methods are given for the identification of alkyl halides as S-alkylisothiouric acid picrates and of aromatic C-nitroso-compounds as 3-arylimino-2-phenylindolenines and *p*-bromoazobenzenes. Tests are recommended for the detection of aromatic hydrocarbons and these tests are shown to be characteristic, as they are given even by highly purified compounds. A colour test for compounds containing the cyclopentadiene nucleus is described.

(i) It was shown (Brown and Campbell, J., 1937, 1699) that alkyl bromides and iodides can be satisfactorily identified as alkylisothiouric acid picrates, and we have now improved and extended the method so that tertiary compounds and chlorides are included. The melting points of the derivatives are more convenient than those of the *N*-alkylsaccharins used by Merritt, Levey, and Cutter (*J. Amer. Chem. Soc.*, 1939, **61**, 15) for the same purpose. Ethylisothiouric acid picrate was obtained from *tert*.-butyl and isovaleryl halides owing to interaction with the solvent, as shown by the formation of methylisothiouric acid picrate when methyl alcohol replaced ethyl alcohol as solvent. Methyl and ethyl chloroformates gave methyl- and ethyl-isothiouric acid picrates respectively.

(ii) Various reagents were investigated for the identification of aromatic C-nitroso-compounds by condensing them with compounds containing reactive methylene groups. The methylene group in 2:7-dibromofluorene (Sieglitz, *Ber.*, 1920, **53**, 1232) is very reactive and condenses readily with C-nitroso-compounds, but on the small scale the products were difficult to purify, probably owing to formation of both anils and nitrones (cf. Schönberg and Michaelis, J., 1937, 627; Bergmann, *ibid.*, p. 1628; Thorneycroft, Thesis, London, 1927; Barrow and Thorneycroft, this vol., p. 770). 2-Phenylindole in presence of alkali condenses readily with nitroso-compounds (Angeli and Morrelli, *Centr.*, 1908, **12**, 605) to form anils, and these are suitable for identifying nitrosobenzene and its *m*- and *p*-substituted derivatives. The azo-compounds formed by condensation of nitroso-compounds with *p*-bromoaniline (Ingold, J., 1925, **127**, 516) were found to be the most suitable derivatives for identification.

(iii) 2:4:5-Trinitrotoluene is a valuable reagent for the alkylamines (Brown and Campbell, *loc. cit.*), but not for aromatic amines. The more easily accessible 2:3:5-trinitro-*p*-xylene is not so reactive with aliphatic amines.

(iv) The fluorescence of many organic compounds (*e.g.*, fluorene) is due to traces of impurities. In view of the use of fluorescence in qualitative work, we purified several aromatic hydrocarbons by chromatographic adsorption to find if thorough purification diminished or removed the fluorescence. This was necessary in view of Dutt's claim (*J. Indian Chem. Soc.*, 1930, **7**, 505) that extensive purification of certain aromatic and heterocyclic compounds removed their fluorescence, which returned only when the compounds were exposed to air. In no case did we observe any change in fluorescence even when some of the compounds studied by Dutt were purified several times by the chromatographic method. Dutt's conclusions seem improbable in the light of other investigations; *e.g.*, he claimed to have obtained pure anthracene which did not fluoresce in ultra-violet light, but Weigert and Jäckh (*Naturwiss.*, 1927, **15**, 124) showed that anthracene is converted into dianthracene in ultra-violet light, the increase in reaction velocity being inversely proportional to the decrease in fluorescence.

(v) The colours obtained by the addition of sulphuric acid, or of sulphuric acid and benzylidene chloride (Lippmann and Pollak, *Monatsh.*, 1902, **23**, 670), to aromatic hydrocarbons were given when the latter were highly purified, and these tests, together with the fluorescence in benzene solution, are valuable aids for detection and identification.

(vi) Vanscheidt (*Chem. Abs.*, 1935, **29**, 2160) gives a test for cyclopentadiene and compounds, such as indene and fluorene, containing the cyclopentadiene nucleus. We have

phenylindole (0.5 g.) were dissolved in alcohol, the solution cooled, and a few drops of alcoholic potassium hydroxide added; a violent reaction occurred. The condensation product which separated was crystallised from alcohol. All formed orange needles, except the nitrosobenzene compound, which formed vermilion prisms.

3-Arylimino-2-phenylindolenines.

Nitroso-compound.	Formula.	M. p.	N, %, found.	N, %, calc.
Nitrosobenzene	$C_{20}H_{14}N_2$	154°	10.5	9.9
<i>o</i> -Chloronitrosobenzene	$C_{20}H_{13}N_2Cl$			
<i>m</i> -Chloronitrosobenzene	"	148	9.25	8.85
<i>p</i> -Chloronitrosobenzene	"	157	9.16	8.85
<i>o</i> -Bromonitrosobenzene	$C_{20}H_{13}N_2Br$			
<i>m</i> -Bromonitrosobenzene	"	169	7.88	7.74
<i>p</i> -Bromonitrosobenzene	"	154	7.93	7.74
<i>o</i> -Nitrosotoluene	$C_{21}H_{15}N_2$			
<i>m</i> -Nitrosotoluene	"	136	9.64	9.46
<i>p</i> -Nitrosotoluene	"	146	9.53	9.46

The following compounds were further analysed: nitrosobenzene derivative (Found: C, 84.5; H, 4.9. $C_{20}H_{14}N_2$ requires C, 85.1; H, 5.0%); *p*-chloronitrosobenzene derivative (Found: C, 76.1; H, 4.1. $C_{20}H_{13}N_2Cl$ requires C, 75.8; H, 4.1%); *p*-nitrosotoluene derivative (Found: C, 84.5; H, 5.7. $C_{21}H_{15}N_2$ requires C, 84.5; H, 5.6%).

p-Nitrosotoluene gave rise, not only to the anil, but also to a high-melting compound formed by the action of the potassium hydroxide used as condensing agent; this was separated from the anil by its insolubility in ether. Tedious separations with benzene gave three fractions, m. p. above 350°, m. p. 209–250°, and m. p. 190–245°. The middle fraction was crystallised several times from benzene and then melted at 215° with the exception of a very small quantity which melted at 250°. Analysis of the compound, m. p. 215° (Found: C, 72.03; H, 5.51; N, 11.77%), is not in good agreement with the results of Reissert (*Ber.*, 1909, **42**, 1371), who had isolated this compound and suggested the termolecular formula $C_{21}H_{19}O_2N_3$ (Calc.: C, 73.01; H, 5.55; N, 12.17%).

Attempts to obtain α -nitrosonaphthalene by the method of Willstätter and Kubli (*Ber.*, 1908, **41**, 1938) gave unsatisfactory results (cf. Neunhoeffer and Liebich, *Ber.*, 1938, **71**, 2247).

Preparation of Substituted p-Bromoazobenzenes.—These were obtained from *p*-bromoaniline and the various nitroso-compounds by Ingold's method (*loc. cit.*) and were purified from glacial acetic acid. 0.1 G. of nitroso-compound can easily be identified by this method.

Nitroso-compound.	Formula.	M. p.	N, %, found.	N, %, calc.
Nitrosobenzene		88°		
<i>o</i> -Chloronitrosobenzene	$C_{12}H_9N_2ClBr$	110	9.74	9.48
<i>m</i> -Chloronitrosobenzene	"	119	9.46	9.48
<i>p</i> -Chloronitrosobenzene	"	190	9.67	9.48
<i>o</i> -Bromonitrosobenzene	$C_{12}H_9N_2Br_2$	104	8.58	8.23
<i>m</i> -Bromonitrosobenzene	"	126	8.16	8.23
<i>p</i> -Bromonitrosobenzene	"	205		
<i>o</i> -Nitrosotoluene	$C_{13}H_{11}N_2Br$			
<i>m</i> -Nitrosotoluene	"	82	10.3	10.2
<i>p</i> -Nitrosotoluene	"	152	10.4	10.2

Preparation of 4:6-Dinitro-N-aryl-m-toluidines.—Prepared from aromatic amines and 2:4:5-trinitrotoluene by the method of Brown and Campbell (*loc. cit.*), these separated from alcohol as orange or yellow needles. Derivatives were obtained from the following amines (m. p.'s in parentheses): aniline (145°), *m*-toluidine (150°), *m*-xylylidine (186°), and *p*-anisidine (139°). The method is not recommended, as amines such as *o*-toluidine did not yield derivatives.

Preparation of 3:5-Dinitro-N-alkyl-p-xylylidines.—Difficulty was experienced in preparing 2:3:5-trinitro-*p*-xylene, for the purchased *p*-xylene contained considerable quantities of the *m*-compound. On oxidation of the xylene with potassium permanganate and esterification of the product with methyl alcohol, methyl terephthalate (m. p. 140°) was obtained, but the alcoholic filtrate after some time deposited the isophthalic ester (m. p. 66°). Nitration of the xylene afforded a mixture which, crystallised from ethyl alcohol, yielded trinitro-*m*-xylene (m. p. 180°), whereas the filtrate on standing gave trinitro-*p*-xylene (m. p. 139°). In testing xylenes it is therefore advisable to use both oxidation and nitration.

2:3:5-Trinitro-*p*-xylene reacted in the same way as 2:4:5-trinitrotoluene towards aliphatic amines, the 2-nitro-group being replaced; e.g., methylamine gave 3:5-dinitro-*N*-methyl-*p*-xylylidine (Found: N, 18.7. $C_9H_{11}O_4N_3$ requires N, 18.7%). The reagent does not react

found this test to be somewhat untrustworthy, but if *p*-dinitrobenzene is added to Vanscheidt's reagent (methyl-alcoholic potassium hydroxide and acetone or pyridine) characteristic green or blue colours are obtained with cyclopentadiene, etc. The mere presence of a methylene group is insufficient to give the test, as negative results were obtained with diphenylmethane, acenaphthene, etc. It was first thought that the test was due to the formation of a potassium salt, but this in itself is insufficient, since indene, phenylacetylene, and 9-phenylfluorene all have the same degree of acidity (Conant and Wheland, *J. Amer. Chem. Soc.*, 1932, 54, 1216) but only indene gives a positive test. Of special interest is truxene, the structure of which has not yet been established. It gives a positive test with our reagent, and this confirms the structure assigned in Beilstein's "Organische Chemie" (cf. Stobbe and Zschoch, *Ber.*, 1927, 60, 457).

EXPERIMENTAL.

Unless otherwise stated, compounds were prepared by standard methods and had the properties given in the literature. M. p.'s were determined in Kofler's apparatus (*Mikrochem.*, 1934, 15, 242). Most of the analyses were done by Mr. W. Brown, Edinburgh.

Preparation of S-Alkylisothiouraea Picrates.—Finely powdered thiourea (1 g.), alkyl halide (1 g.), and ethyl alcohol (10 c.c.) were refluxed for a period depending on the nature of the alkyl halide (see following table). Picric acid (1 g.) was then added, and the mixture heated until a clear solution was obtained and cooled. If no precipitate separated, a few drops of water were added. The picrates crystallised from alcohol in yellow needles or prisms. In the majority of cases the method can easily be applied with 0.2 g. of alkyl halide.

S-Alkylisothiouraea Picrates.

Alkyl halide.	Formula.	M. p.	Time.	N, %, found.	N, %, calc.
Methyl iodide		224°	5 mins.		
Ethyl iodide		188	5 mins.		
Ethylene dibromide		260	15 mins.		
<i>n</i> -Propyl bromide		177	5 mins.		
<i>n</i> -Propyl chloride *	$C_{10}H_{13}O_7N_5S$	176	5 hrs.	19.9	20.2
<i>iso</i> Propyl bromide		196	3 hrs.		
Propylene dibromide *	$C_{11}H_{15}O_7N_5S_2$	232	40 mins.	23.2	23.3
<i>n</i> -Butyl bromide		177	5 mins.		
<i>n</i> -Butyl chloride	$C_{11}H_{15}O_7N_5S$	177	2 hrs.	19.5	19.4
<i>iso</i> Butyl iodide		167	10 mins.		
<i>sec</i> -Butyl iodide *		166	10 mins.		
<i>tert</i> -Butyl iodide †	$C_{11}H_{15}O_7N_5S$	188	3 hrs.	20.8	21.0
<i>iso</i> Butylene dibromide *	$C_{12}H_{17}O_7N_5S_2$	223	1 hr.	22.1	22.5
<i>n</i> -Amyl bromide		154	20 mins.		
<i>n</i> -Amyl chloride	$C_{12}H_{17}O_7N_5S$	154	2 hrs.	19.0	18.7
<i>iso</i> Amyl bromide		173	20 mins.		
<i>iso</i> Amyl chloride *	$C_{12}H_{17}O_7N_5S$	173	2 hrs.	19.0	18.7
<i>sec</i> -Amyl bromide		157	40 mins.		
<i>iso</i> Valeryl chloride †	$C_9H_{11}O_7N_5S$	187	3 hrs.	21.0	21.0
<i>n</i> -Hexyl bromide		157	20 mins.		
<i>n</i> -Heptyl bromide	$C_{14}H_{21}O_7N_5S$	142	20 mins.	17.4	17.4
<i>n</i> -Octyl bromide	$C_{15}H_{23}O_7N_5S$	134	20 mins.	16.5	16.8
Cetyl iodide	$C_{28}H_{59}O_7N_5S$	137	3 hrs.	13.4	13.2
Allyl chloride	$C_{10}H_{11}O_7N_5S$	155	5 mins.	20.5	20.3
Trimethylene dibromide	$C_{11}H_{15}O_7N_5S_2$	229	5 mins.	23.1	23.3
α -Phenylethyl bromide	$C_{15}H_{15}O_7N_5S$	167	5 mins.	17.4	17.1
β -Phenylethyl bromide	$C_{15}H_{15}O_7N_5S$	139	5 mins.	16.9	17.1
<i>o</i> -Bromobenzyl bromide	$C_{14}H_{12}O_7N_5BrS$	222	5 mins.	15.1	14.8
<i>m</i> -Bromobenzyl bromide	$C_{14}H_{12}O_7N_5BrS$	205	5 mins.	14.9	14.8
<i>p</i> -Bromobenzyl chloride	$C_{14}H_{12}O_7N_5BrS$	219	5 mins.	14.8	14.8
<i>o</i> -Chlorobenzyl bromide	$C_{14}H_{12}O_7N_5ClS$	213	5 mins.	15.6	16.3
<i>m</i> -Chlorobenzyl bromide	$C_{14}H_{12}O_7N_5ClS$	200	5 mins.	16.3	16.3
<i>p</i> -Chlorobenzyl bromide	$C_{14}H_{12}O_7N_5ClS$	194	5 mins.	16.4	16.3
Methyl chloroformate ‡		224	30 mins.		
Ethyl chloroformate ‡		187	30 mins.		

* Small yield.

† S-Ethylisothiouraea picrate.

‡ S-Methylisothiouraea picrate.

Two compounds were further analysed: *m*-chlorobenzylisothiouraea picrate (Found: C, 39.3; H, 3.4. $C_{14}H_{12}O_7N_5ClS$ requires C, 39.1; H, 2.8%), and *o*-bromobenzylisothiouraea picrate (Found: C, 35.8; H, 2.7. $C_{14}H_{12}O_7N_5BrS$ requires C, 35.4; H, 2.5%).

Preparation of 3-Arylimino-2-phenylindolenines.—The nitroso-compound (0.5 g.) and 2-

tested was added; 3 drops of methyl-alcoholic potash (3 c.c. of alcohol containing 3 drops of 4N-alkali) were added, the colour noted, and then more alcoholic potash was added until no further change of colour occurred.

Negative results were obtained with 9-phenylfluorene, diphenylmethane, triphenylmethane, phenylacetylene, triphenylcarbinol, and acenaphthene.

Preparation of 2:4-Dinitrobenzoic Acid.—The method given by Brown and Campbell (*loc. cit.*) is not reliable (Storrie, private communication), the yield being profoundly affected by the nature and concentration of the nitric acid. Storrie's method (J., 1937, 1746) therefore remains the best available.

We wish to thank Prof. J. W. Cook for samples of fluorene derivatives, the Moray Fund for a grant, and the Carnegie Trust for the Universities of Scotland for a teaching fellowship awarded to one of us (N. C.).

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readily with many aliphatic amines, and is therefore not to be recommended for this class of compound.

Fluorescence and Colour Tests of Aromatic Hydrocarbons.—All fluorescence observations were made with ultra-violet light from a Hanovia mercury lamp provided with a filter to eliminate visible waves.

Several hydrocarbons were thoroughly purified by chromatographic adsorption, a 30-in. column packed with Brockmann's aluminium oxide being used. In some cases several purifications were effected. Fluorene (0.2 g. in 200 c.c. of benzene; developer, benzene) was obtained from the filtrate as a non-fluorescing compound. Naphthalene (0.5 g. in 250 c.c. of light petroleum; developer, same solvent) was obtained in the filtrate, and had a purple fluorescence. Anthracene [0.2 g. in 750 c.c. of light petroleum (b. p. 40–60°); developer, same solvent] was obtained in the filtrate and had a purple fluorescence; from the column, dianthracene, m. p. 230°, was obtained. When the purification was performed in the dark, no dianthracene was detected. Chrysene [light petroleum (b. p. 40–60°) as solvent and developer] was isolated from the filtrate and had a bright purple fluorescence. Pyrene [0.2 g. in 10:1 benzene–light petroleum (b. p. 40–60°); developer, 3:1 benzene–light petroleum] was obtained from the filtrate as a pure white substance (cf. Clar, *Ber.*, 1936, 69, 1684) with a vivid light green fluorescence; from the column, a minute amount of a yellow compound was obtained which gave colour tests for anthracene. 1:2-Benzanthracene (benzene as solvent and developer) was obtained from the filtrate and gave a purple fluorescence. In the treatment of 2:3-benzanthracene (0.2 g. in 500 c.c. of benzene; developer, benzene), the column became yellow and the side exposed to the window light turned orange. The orange compound was identified as 2:3-naphthaquinone, m. p. 188° (lit., 194°), by the red colour it gave with concentrated sulphuric acid. When the experiment was performed in the dark, the filtrate yielded the pure hydrocarbon with a slight green fluorescence, and from the tube some of the quinone was isolated.

The colours obtained with the purified hydrocarbons and sulphuric acid, and benzylidene chloride and sulphuric acid, were the same as those given by the unpurified compounds. The latter test is reliable only when standard conditions are used: one drop of benzylidene chloride is dissolved in benzene (10 c.c.), a few mg. of the compound added, and the mixture shaken. The colours obtained were in some instances different from those observed by Lippmann and Pollak (*loc. cit.*).

Benzylidene chloride test.

Compound.	Colour.	Compound.	Colour.
Diphenylmethane	Yellow	1:2:5:6-Dibenzfluorene	Yellowish-green
Diphenyl	Carmine-red	Phenanthrene	Violet
Retene	Violet	Perylene	Dark purple
Fluorene	Carmine-red	1:2-Benzanthracene	Reddish-brown
9-Phenylfluorene	Carmine-red	9:10-Benzphenanthrene	Purple
1:2-Benzfluorene	Green	Fluoranthene	Purple
3:4-Benzfluorene	Emerald-green		

No characteristic colours were obtained with benzopyrene, dibenzyl, hydrindene, 2:3-benzanthracene, or truxene. Quinones did not respond to the test.

Detection of cyclopentadiene Derivatives.—*p*-Dinitrobenzene (0.2 g.) was dissolved in pyridine (preferably) or acetone (100 c.c.), and to 3 c.c. of this solution a little of the compound to be

Colour test for cyclopentadiene derivatives.

Compound.	Solvent.	
	Acetone.	Pyridine.
cyclopentadiene	Greenish-yellow	Greenish-yellow
Dicyclopentadiene	—	Emerald-green
Indene	Emerald-green	Emerald-green
Fluorene	Blue → green	Emerald-green
2-Nitrofluorene	Prussian-blue	Greenish-blue
2-Bromofluorene	Blue → green	Dark green
2:7-Dibromofluorene	Prussian-blue → emerald-green	Greenish-blue
7-Bromo-2-nitrofluorene	Prussian-blue	Prussian-blue
2-Bromo-3-nitrofluorene	Blue → dark green	Prussian-blue
1:2-Benzfluorene	—	Green
3:4-Benzfluorene	Dark green	Emerald-green
1:2:5:6-Dibenzfluorene	Emerald-green	Emerald-green
Truxene	Dirty green	Emerald-green

THE STRUCTURE OF THE NITROINDAZOLES AND THEIR N-METHYL DERIVATIVES

BY
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AND
GEORGE DODDS

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26. *The Structure of the Nitroindazoles and their N-Methyl Derivatives.*

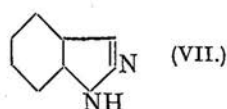
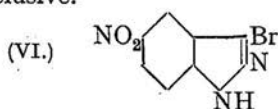
By IAN M. BARCLAY, NEIL CAMPBELL, and GEORGE DODDS.

The bromine reactivity of the *N*-methyl derivatives of three 3-bromonitroindazoles has been measured, and the results discussed in relation to the structures of indazole and its derivatives. Evidence is given for the quinonoid formula for 2-alkylindazoles. There are indications that indazole resembles in structure the 1-alkyl compounds, and this is confirmed by absorption-spectra measurements.

The validity of the Auwers rule for the alkylation of indazoles is questioned.

THE structure of indazole and its derivatives has been intensively studied by Auwers and others (see, *e.g.*, Auwers and Duesberg, *Ber.*, 1920, 53, 1179; Auwers and Schwegler, *ibid.*, p. 1211; Auwers, *Annalen*, 1924, 437, 70; Meisenheimer and Diedrich, *Ber.*, 1924, 57, 1715; Fries, *Annalen*, 1927, 454, 303) both by chemical and by physical methods. By analogy with other heterocyclic compounds there can be little doubt that indazole

2-derivative. Hence the isomer, m. p. 163°, is 5-nitro-1-methylindazole. This is the opposite of the formula assigned by Fries (*loc. cit.*), who, however, noted that his evidence was inconclusive.



The small reactivity of 3-bromo-5-nitroindazole indicates that structure (VI) is the main contributing form, and suggests that the corresponding form (VII) holds for indazole. This is in agreement with Auwers's conclusion (previous reference) that indazole closely resembles the 1-alkyl derivatives, *e.g.*, (I). Further support for this conclusion is provided by the absorption spectra of indazole, 5- and 6-nitroindazoles, and their *N*-methyl-

FIG. 1.

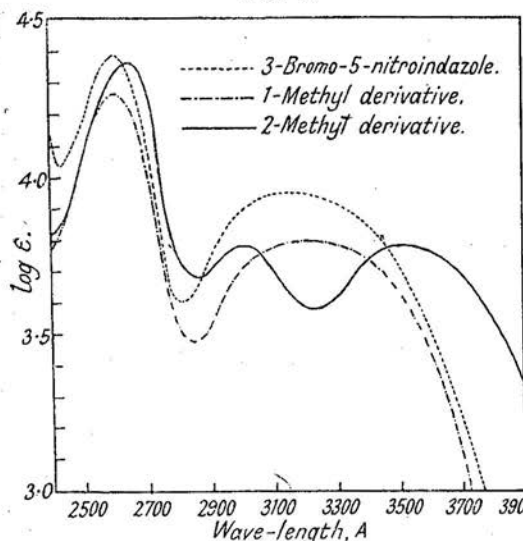
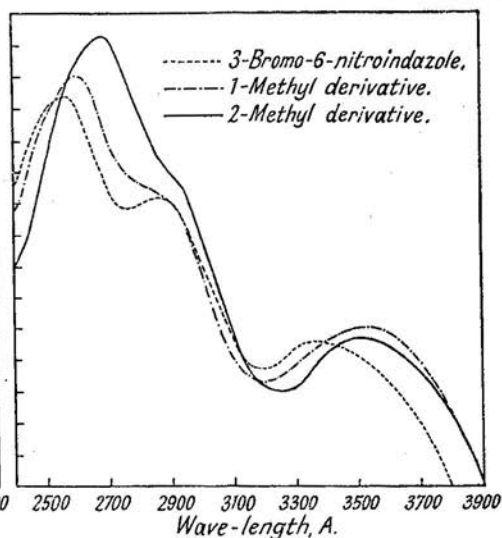
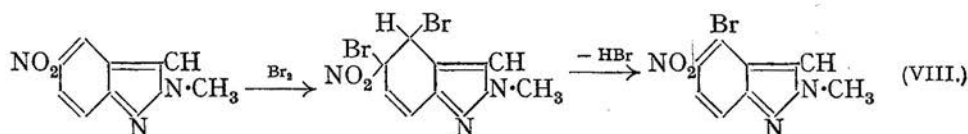


FIG. 2.



derivatives. Little can be deduced from the curves of 6-nitroindazole, but in the other two cases there is a close similarity between the parent indazole and its 1-methyl derivative but a decided difference from the 2-methyl isomer.

Following other workers in the field (*e.g.*, Witt, Noetting, and Grandmougin, *Ber.*, 1890, 23, 3635), we have assumed throughout that bromination of indazoles occurs in position 3. There is, however, the possibility that, if (say) 5-nitro-2-methylindazole has the quinonoid structure, addition of bromine, followed by elimination of hydrogen bromide (*cf.* J., 1931, 3308), might occur to give 4-bromo-5-nitro-2-methylindazole (VIII):

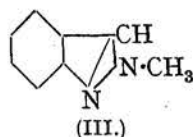
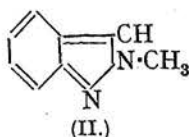
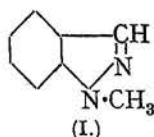


(The bromine in this compound would be reactive to piperidine and its reactivity would sustain the argument for the quinonoid form.) Formation of the 4-bromo-compound is possible, but in our opinion extremely unlikely in view of the reactive 3-position of indazoles and the presence of the nitro-group in the benzene ring. Further, if bromination did occur preferentially in the 4-position, further bromination to give the 3:4-dibromo-compound would be expected. No indication of this was found, although in the several cases investigated excess bromine was used.

Attempts to prepare 5-nitro-1-methylindazole from the methylhydrazone of 2-chloro-

and its derivatives are resonance hybrids, the resonance being largely due to that of the benzene nuclei (cf. Pauling and Sherman, *J. Chem. Physics*, 1933, 1, 606), though the necessary data are lacking to test the matter quantitatively. The present paper deals mainly with the structure of the heterocyclic ring.

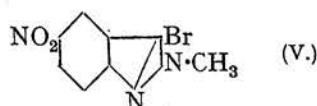
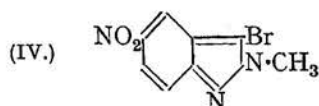
1-Methylindazole is represented without ambiguity by (I), but the structure of the 2-compound has not yet been settled. Auwers (*loc. cit.*, 1924) rejects (III) and accepts



(II), pointing out the difficulty of constructing a molecule with a three-membered ring. Meisenheimer (*loc. cit.*) supports this view, but Fries (*loc. cit.*) prefers (III), as the 2-alkylindazoles are colourless and show no quinonoid properties. Our results show that one of the forms contributing to the hybrid is the quinonoid structure.

It is known that, if a bromo-group is separated from a nitro-group by a double bond or conjugated system of double bonds, the bromine is reactive towards piperidine (*e.g.*, McLeish and Campbell, *J.*, 1937, 1103) and this method of double-bond detection is applied in the present paper to derivatives of the nitroindazoles.

Consideration of the possible formulæ for the methyl derivatives of all the 3-bromo-*x*-nitroindazoles shows that reactive bromine will be found only in one compound, *viz.*,



3-bromo-5-nitro-2-methylindazole and then only if it possesses a quinonoid structure as one of the contributory forms (IV). That this is indeed the case is shown by the following table giving the removal of bromine by piperidine under different conditions.

Compound.	Removal of bromine, %.		
	i.	ii.	iii.
3-Bromo-4-nitroindazole		0	
3-Bromo-4-nitro-1-methylindazole	0	0	
3-Bromo-4-nitro-2-methylindazole	0	0	
3-Bromo-5-nitroindazole	0	4	0
			1
3-Bromo-5-nitromethylindazole, m. p. 188°	2	30	44
			45
3-Bromo-5-nitromethylindazole, m. p. 225°	0	0	0
			0
3-Bromo-6-nitroindazole			0
			2
3-Bromo-6-nitro-1-methylindazole	0	0	0
			2
3-Bromo-6-nitro-2-methylindazole	0	0	0
			0

Col. i. Piperidine at 45° for 1 hour.
 Col. ii. Piperidine at 45° for 24 hours.
 Col. iii. Piperidine at 95° for 3 hours.

It therefore is necessary to assign an *o*-quinonoid structure to 3-bromo-5-nitro-2-methylindazole, and by analogy it is probable that all 2-alkylindazoles possess this structure. This conclusion is supported by Auwers's refractivity measurements (*Annalen*, 1937, 527, 291). It might be argued that the three-membered ring formula (V) would account for the reactivity by the N_1-C_3 bond, but if this were so the 2-alkyl derivatives of all 3-bromoindazoles should show bromine reactivity. This is not the case.

The results of the bromination of the 5-nitromethylindazoles were as follows: methyl compound, m. p. 163° → bromo-compound, m. p. 225°; methyl compound, m. p. 129° → bromo-compound, m. p. 188°. As the bromo-compound, m. p. 188°, is reactive, it must be methylated in the 2-position, and hence its precursor, m. p. 129°, must also be the

promised experimental details were never published. Cohen and Dakin (J., 1902, 81, 26) could not obtain the amino-compound directly. *o*-Toluic acid was therefore nitrated, and the resulting mixture separated by the rather unsatisfactory method of Scherpenzeel (*Rec. Trav. chim.*, 1901, 20, 173). *p*-Nitrobenzyl 4-nitro-*o*-toluate formed leaflets (acetic acid), m. p. 149° (Found: N, 8.6. $C_{15}H_{12}O_6N_2$ requires N, 8.8%), and *p*-nitrobenzyl 6-nitro-*o*-toluate, prisms (alcohol), m. p. 108–114° (Found: N, 9.3%). 6-Nitro-*o*-toluamide gave a poor yield of 6-nitro-*o*-toluidine by the Hofmann reaction, but Curtius degradation of the azide gave good results. The acid chloride of 6-nitro-*o*-toluic acid (11 g.) was dissolved in benzene (100 c.c.), and powdered sodium azide (3 g.) was slowly added, the solution being vigorously shaken. The solution was finally heated gently and then boiled with an equal volume of concentrated hydrochloric acid for 4 hours. The benzene was removed, and the hydrochloride of 6-nitro-*o*-toluidine converted into the base by trituration with concentrated aqueous ammonia; crystallised from alcohol, it had m. p. 91° (lit., 92°); yield, 40%. 4-Nitroindazole was obtained by Noeltling's method (*Ber.*, 1904, 37, 2582). The indazole was methylated by a quicker method than that of Auwers and Frese (*Ber.*, 1925, 58, 1369). 4-Nitroindazole (4 g.), potassium hydroxide (3 g.), methyl iodide (9 g.), and methyl alcohol (25 c.c.) were heated under reflux for 4 hours, and the solution poured into water. The precipitate obtained was dried on porous plate, dissolved in ether, and separated by the method of Auwers and Frese (*loc. cit.*). 4-Nitro-1-methylindazole, crystallised from light petroleum (b. p. 80–100°), had m. p. 136° (lit., 138–139°); yield, 0.8 g. The 2-methyl compound, crystallised from water, had m. p. 98° (lit., 101–103°); yield, 0.3 g. The methyl derivatives were brominated by suspending them in dilute hydrochloric acid, adding bromine water, and stirring vigorously for $\frac{1}{2}$ hour. The precipitate was washed with water, and crystallised from alcohol. 3-Bromo-4-nitro-1-methylindazole had m. p. 216–220° (Found: Br, 29.4. $C_8H_6O_2N_3Br$ requires Br, 31.2%). There was only sufficient of the 2-methyl isomer, m. p. 195–199°, for the reactivity measurements.

3-Bromo-5-nitroindazole.—5-Nitroindazole (1 g.) was brominated in dilute hydrochloric acid as above. The precipitate was boiled with water to remove any unchanged nitroindazole, and obtained in colourless, cubic prisms (alcohol), m. p. 221°; it sublimes in the same form; yield, 1 g. (Found: Br, 31.3. $C_7H_4O_2N_3Br$ requires Br, 33.0%).

N-Methyl Derivatives of 3-Bromo-5-nitroindazole.—The 5-nitromethylindazoles, prepared by the method of Fries (*loc. cit.*), were obtained as colourless needles when crystallised from light petroleum (b. p. 80–100°). From the isomer of m. p. 163°, 3-bromo-5-nitro-1-methylindazole was obtained as pale yellow needles (alcohol-acetic acid) or colourless needles (light petroleum, b. p. 80–100°), m. p. 225°; it sublimes in prisms (Found: Br, 30.6. $C_8H_6O_2N_3Br$ requires Br, 31.2%). From the other isomer, m. p. 129°, 3-bromo-5-nitro-2-methylindazole was obtained in yellow needles (alcohol) or pale yellow needles (light petroleum, b. p. 80–100°), m. p. 188°, subliming in cubic prisms (Found: Br, 30.2%).

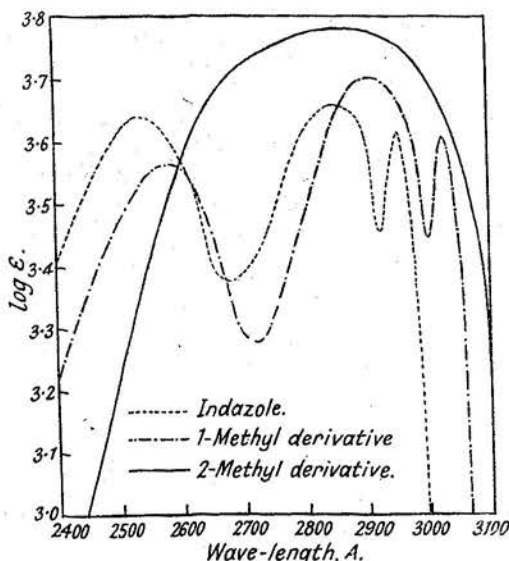
Attempted Preparation of 5-Nitro-1-methylindazole.—2-Chloro-5-nitrobenzaldehyde (Erdmann, *Annalen*, 1893, 272, 153) gave the 2:4-dinitrophenylhydrazones as orange prisms (tetralin) or needles (methyl alcohol), m. p. 280° (decomp.) (Found: N, 19.1. $C_{13}H_8O_6N_2Cl$ requires N, 19.1%). 2-Chloro-5-nitrobenzaldehydemethylhydrazone was prepared by heating the aldehyde (0.85 g.), methylhydrazine sulphate (0.7 g.), and crystalline sodium acetate (0.7 g.) in aqueous alcohol for 10 minutes. Water was added, and the precipitate crystallised first from aqueous methyl alcohol and then from light petroleum (b. p. 60–80°); yellow needles, m. p. 121–122°, subliming (Found: N, 20.2. $C_8H_6O_2N_3Cl$ requires N, 19.7%). All efforts to close the ring in this compound with potassium hydroxide were unsuccessful.

N-Methyl Derivatives of 6-Nitroindazole.—These were prepared from 6-nitroindazole by the method used for the 5-compound. Auwers and Schwegler (*loc. cit.*) obtained only one of the isomers in the pure state. We effected separation of the mixture by fractional crystallisation from methyl alcohol, 6-nitro-2-methylindazole separating from the hot solution in yellow prisms, m. p. 160° (lit. 159–160°). Addition of water to the filtrate gave the 6-nitro-1-methylindazole, which separated as colourless needles from light petroleum (b. p. 60–80°), m. p. 125° (lit., 105–108°) (Found: C, 54.5; H, 3.9. Calc. for $C_8H_6O_2N_3$: C, 54.3; H, 3.9%). The yield of the 2-methyl is three times that of the 1-methyl derivative.

N-Methyl Derivatives of 3-Bromo-6-nitroindazole.—These were prepared either by methylation of 3-bromo-6-nitroindazole (5.0 g.) or by bromination of the 6-nitromethylindazoles by methods given above. In the first case, the isomers were separated by ether. The insoluble isomer was crystallised three times from ethyl alcohol, yellow needles, m. p. 175°; yield 2.5 g. (50%) (Found: Br, 31.6. $C_8H_6O_2N_3Br$ requires Br, 31.2%). As the compound is identical with that obtained by the bromination of 6-nitro-2-methylindazole, it is 3-bromo-6-nitro-2-methyl-

5-nitrobenzaldehyde were unsuccessful. This is rather surprising in view of the ease with which Fries (*loc. cit.*) effected ring-closure of the phenylhydrazone of 2-chloro-5-nitrobenzophenone, though on the other hand Meyer (*Ber.*, 1893, 26, 1253) could not effect closure of a ring in the phenylhydrazone of 2-chloro-5-nitrobenzaldehyde.

FIG. 3.



Analyses were done by Drs. Weiler and Strauss, Oxford, and Mr. Brown, Edinburgh. The reactivity measurements were carried out as in previous papers (Campbell and McLeish, *loc. cit.*).

Spectroscopic Measurements.—A Bellingham and Stanley "medium" quartz spectrograph was used, giving the spectrum from 2400 Å. to the red region on a 10 × 4 in. plate. The solutions were 0.0001M in ethyl alcohol. An iron spark was used as the source of light, and by using the rotating-sector method, a quantitative determination of the absorption curves was obtained.

Indazole.—Precise instructions are lacking for the preparation of indazole by the method of Jacobson and Huber (*Ber.*, 1908, 41, 2574). The following method was finally adopted (cf. Auwers, *Ber.*, 1919, 52, 1335; Haworth and Hey, *J.*, 1940, 365). Benz-*o*-toluidide (20 g.) was dissolved in a hot mixture of acetic acid (50 c.c.) and acetic anhydride (50 c.c.) and rapidly cooled with stirring to obtain fine crystals. The mixture was then cooled to 3°, and nitrous fumes passed in at the rate of one or two bubbles per second. A deep green colour was obtained after about 20 mins., the temperature of the solution never having exceeded 10°. Immediately a clear solution was obtained it was poured into water (100 g.) and ice (100 g.). The oil which separated soon solidified on being stirred. The precipitate was washed with cold water until only a faint odour of acetic acid remained, pressed on tile, and dried at room temperature for 2 hours. The nitroso-compound (characterised by its "flash" on heating) was added to sodium-dried benzene (150 c.c.), the solution kept overnight, refluxed for 1 hour, and 100 c.c. of benzene distilled off. The solution was separated from benz-*o*-toluidide, shaken with sodium carbonate solution (50 c.c.), washed with water, and extracted with 2N-hydrochloric acid (100 c.c.). Treatment with sodium hydroxide gave indazole, which, crystallised from hot water, had m. p. 146° (lit., 146°); yield of pure compound, 1 g. The *picrate* (Auwers and Duesberg, *loc. cit.*) crystallised from ether in yellow needles, which were converted into orange prisms on standing in suspension; m. p. 136° (lit., 136–137°). It had not previously been analysed (Found: N, 19.5. $C_{13}H_9O_7N_5$ requires N, 20.2%).

N-Methyl Derivatives of 3-Bromo-4-nitroindazole.—Great difficulty was experienced in preparing 6-nitro-*o*-toluidine required for making 4-nitroindazole. The preparation from 2:4:6-trinitrotoluene (Tiemann, *Ber.*, 1870, 3, 218; Beilstein, *ibid.*, 1880, 13, 243) gave very poor yields of 2:6-dinitro-4-aminotoluene, although many modifications of the method were tried, and removal of the amino-group gave only a 5% yield of the nitrotoluidine. Korner and Cortardi (*Atti R. Accad. Lincei*, 1916, 25, 339) claimed a 60% yield by the reduction but the

Auwers and Duesberg (*loc. cit.*) formulated the rule that alkylation of indazoles in alkaline solution takes place mainly in the 1-position. Exceptions to the rule are known (e.g., Auwers and Dereser, *Ber.*, 1919, 52, 1340). We have found other exceptions in the methylation of 6-nitroindazole and 3-bromo-6-nitroindazole, and are inclined to doubt the general validity of this rule, as the quantitative separation of the isomers produced is a matter of difficulty.

EXPERIMENTAL.

Unless otherwise stated, the methods of preparation, properties, and purification of compounds used are those given in the literature. The purity of the compounds was checked by the sharpness of their m. p.'s on the Kofler micro-apparatus (*Mikrochem.*, 1934, 15, 242).

indazole. The soluble 1-methyl isomer was crystallised several times from methyl alcohol, forming colourless, elongated prisms, m. p. 156°; it sublimed in compact prisms. Yield 0.7 g. (14%) (Found: Br, 31.5%).

Colour of Nitroindazole Derivatives.—Some of the nitroindazole derivatives are stated in the literature to be coloured (*e.g.*, Fries, *loc. cit.*). It was found, however, that when crystallised from light petroleum most of them were colourless, the exceptions being 3-bromo-5- and -6-nitro-2-methylindazole (both yellow).

We wish to thank several of the advanced students in the Department for preparing intermediates, the Carnegie Trust for the Universities of Scotland for a teaching fellowship to one of us (N. C.), and the Moray Fund for a grant.

UNIVERSITY OF EDINBURGH.

[Received, November 21st, 1940.]

THE FINE STRUCTURE OF CONDENSED
RING COMPOUNDS.

By

NEIL CAMPBELL, B.Sc., Ph.D.

Thesis submitted for the Degree of Doctor
of Science.

May 1941.

University of Edinburgh.

This thesis deals with the fine structure of the aromatic hydrocarbons and the heterocyclic compound indazole. The author's contributions are given in the attached reprints from the Journal of the Chemical Society, while the typescript gives an account of the theories involved as well as some work not yet published. Certain considerations outlined in the publications are expanded.

Much of the experimental work was done by graduates, and the author gratefully acknowledges his indebtedness to them. His own contribution consisted chiefly in preliminary experimentation and checking and extending the results obtained by his co-workers.

Part I gives a general survey of the subject, and Part II deals more particularly with those topics related to the author's work.

P A R T I.

To what extent are the properties of the benzene ring modified when annealed to other rings in condensed ring systems? Are the nuclei in naphthalene, for instance, true benzene rings?



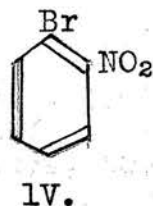
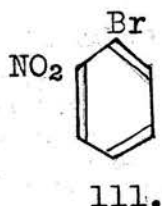
This problem which involves both the exact meaning of the terms "double bond" and "bond distribution" has attracted many workers and is the subject of this thesis. In particular, derivatives of the following compounds have been studied - naphthalene, hydrindene, tetralin, acenaphthene, fluorene, diphenyl, and indazole.

Benzene.

It is readily understandable that the structure of benzene is of fundamental importance, and important advances have recently added to our knowledge of this "key" compound (see, for example, the section on resonance). The brilliant intuition of Kekulé led to the conception of benzene as a regular hexagon of six

equivalent carbon atoms (Bull. Soc. Chim., 1865, 3, 98; Annalen, 1866, 137, 129). The Kekulé formula has been the foundation of aromatic chemistry, and though not completely satisfactory, was until recently the formula most acceptable to organic chemists. Indeed, at the present time, it may still be employed with advantage, provided certain reservations are kept in mind. The formula's most serious flaw is that it does not account for the high stability exhibited by benzene. This led to the ingenious theory of Thiele which, however, never completely satisfied organic chemists owing to the difficulty of attaching a scientific meaning to the term "partial valence".

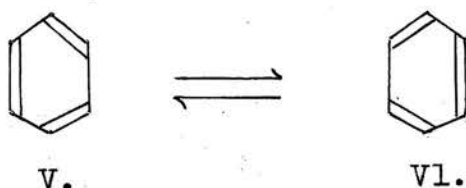
An attendant question was immediately raised by the Kekulé formula — are the 2- and 6-positions equivalent in a disubstituted benzene? For example, are two o-bromonitrobenzenes (III and IV) capable of existence?



In the first case the two substituents are separated by a single bond, and in the second by a double bond.

Victor Meyer (Annalen, 1870, 156, 293) very reasonably suggested that this subtle difference in structure was

insufficient to result in two distinct chemical entities, and concluded that the formulae represented one and the same compound. Kekulé strongly opposed this point of view and advanced the hypothesis that the two benzene forms oscillate, giving rise to tautomerism ($V \rightleftharpoons VI$) (Annalen, 1872, 162, 85).

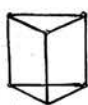


This was generally accepted and when one considers the triumphs of the organic chemist in the last seventy-five years it is not difficult to agree with Hofmann's verdict (Ber., 1890, 23, 272): "Er (Kekulé) wird Ihnen das Benzol also die Fackel schildern, welche den Pfad der in das Gebiet der chemischen Erscheinungen Eindringenden erhielt hat, als das leuchtende Sternbild nach welchem die chemischen Forscher auch kommender Zeiten dankbar ihren Curs steuern werden".

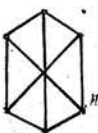
Other formulae have been advanced but they have not the same appeal and some have quite definitely been shown to be erroneous. For instance, the prismatic formula of Ladenburg (VII) was disproved by a number of experimental facts, the chief of which is the plane structure of benzene and its derivatives as shown by X-ray studies. Beyond dispute the six carbon atoms of the benzene molecule and the attached hydrogen atoms

or substituent groups lie in one plane. (Bergmann and Mark, Ber., 1929, 62, 750. Bragg, Proc. Roy. Soc., 1922, 34, 33; 1923, 35, 167. Lonsdale, Trans. Far. Soc., 1929, 25, 352. Robertson, Chem. Reviews, 1935, 16, 434. Jones, Trans. Far. Soc., 1935, 31, 1036).

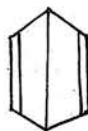
Other formulae, such as those of Claus and Dewar (VIII and IX), contain a para-bond.



VII.



VIII.



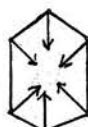
IX.

As pointed out by Fieser (Gilman's Organic Chemistry, Vol. I, p. 59), the length of the para-bond would be 2.80 \AA , exactly twice the distance between adjacent carbon atoms in the ring. When it is considered that the C-C distance in diamond is 1.54 \AA , it is difficult to attach the ordinary meaning of the word bond to the para-linkage.

The Armstrong-Baeyer (X or XI) formula has attracted some notable adherents (e.g., Pope, Introduction to "Practical Organic Chemistry" by Mann and Saunders)



X.



XI.

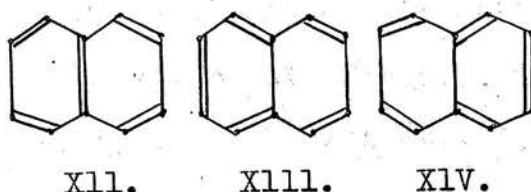
but, as in the case of Thiele's free valencies, it is

difficult to attach any real meaning to the centric bonds.

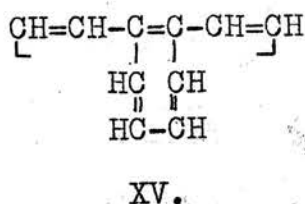
The Kekulé formula therefore has dominated aromatic chemistry and has been used in theoretical considerations of compounds such as benzene, naphthalene, etc.

Naphthalene.

The structure of naphthalene was early considered, and in particular the three structures (XII, XIII, XIV):-

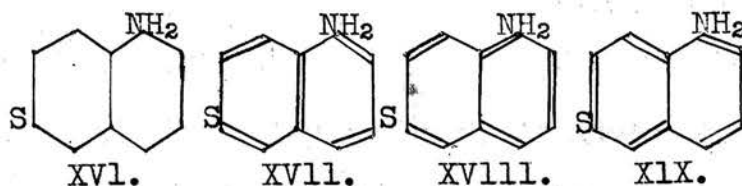


The most favoured is the symmetrical formula of Erlenmeyer (Annalen, 1866, 137, 340) who wrote his formula as follows (XV), but undoubtedly intended naphthalene to be represented by two benzene rings with a double bond in common (XII) .



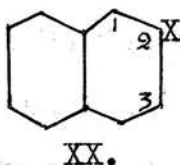
Erdmann (Annalen, 1893, 275, 189), as the result of some investigations on the naphthylamine sulphonic acids, concluded that naphthalene is represented by dynamic isomerism of the three structures, and used

this idea to represent three different 1-amino-6-naphthalene sulphonic acids (XVI - XIX)



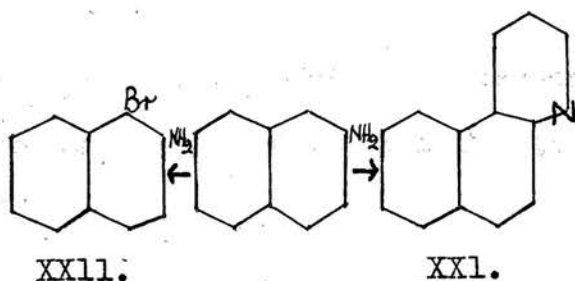
Here, quite definitely, the idea of fixed structures is presented, but as the experimental evidence was erroneous, unsymmetrical formulae have not generally been adopted (cf., however, Ufimzew, Ber., 1936, 69, 2188). Further, critical investigations of the structure of naphthalene have favoured decidedly the symmetrical structure. The evidence for this "fixed structure" merits some consideration.

Marckwald (Annalen, 1893, 274, 331: *ibid.*, 1894, 279, 1) was the first to stress the difference of the 1- and 3-positions in certain 2-substituted naphthalenes (XX)



Positions 1 and 3 are ortho to the substituent X but are by no means equivalent. This is clearly shown by considering β -naphthylamine and β -naphthol.

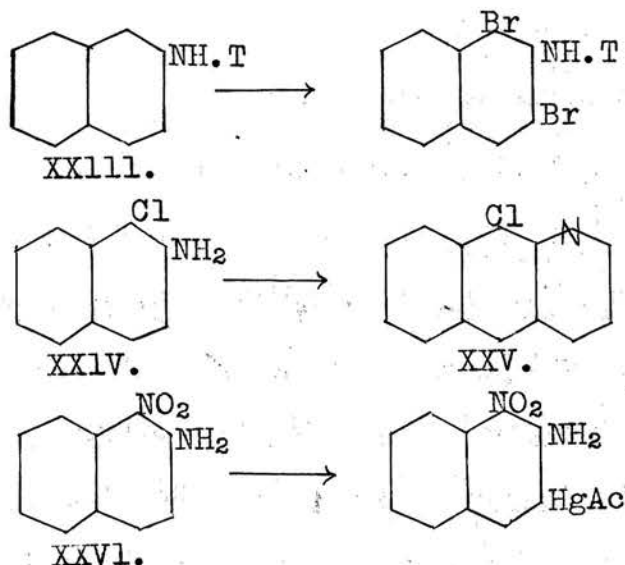
β -Naphthylamine undergoes the Skraup reaction to give only the ang.-quinoline (XXI) and not the linear compound (Skraup and Fischer, Monats., 1884, 5, 523)



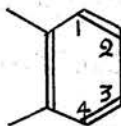
Bromination of β -naphthylamine derivatives occurs in the 1-position (e.g., Cosmer, Ber., 1881, 14, 59) and when further substitution occurs it is only in rare cases in position-3 (see below). Marckwald concluded from those and other experiments that in 2-substituted naphthalenes the 3-position is generally inactive, and that this difference is due to the existence of double bonds in the 1:2 and 3:4 positions, whilst a single bond links C_2 and C_3 . This results from the inhibition of bond oscillation and gives rise to the fixed Erlenmeyer structure. To quote from Marckwald's second paper: "Die Kekule'sche Benzolhypothese in Verbindung mit der Aufnahme, dass in den mehrfachen Ringsystemen die Oscillation aufgehoben ist, steht mit keiner bisher aufgefunden Thatsache in widerspruch".

Marckwald's pioneer work is undoubtedly of prime importance but as the author himself indicated, the results are not entirely conclusive. In certain cases "abnormal" reactions occur in which the 3-position is reactive. For instance, β -p-toluenesulphonamido-naphthalene (XXIII) brominates in the 3- as well as the 1-position (Bell, J., 1932, 2732); 1-chloro-2-naphthylamine (XXIV) yields the linear quinoline (XXV) (Fries,

Annalen, 1935, 576, 285); and 1-nitro-2-naphthylamine (XXVI) mercurates in the 3-position (Hodgson and Elliot, J., 1939, 345)

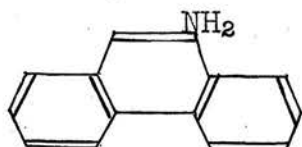


One criticism of Marckwald's conclusions is that the reactions used, although they differentiate between the 1:2- and 2:3-linkages, do not necessarily denote the presence of the bond-system

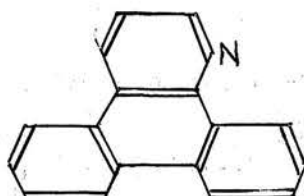


in the naphthalene molecule. True, bromination is frequently regarded as addition at a double bond in the benzene ring, but the mechanism of substitution is only imperfectly understood. Our understanding of the mechanism of the Skraup reaction is also incomplete, though the fact that 9-aminophenanthrene (XXVII) readily

gives 9:10-phenanthroquinoline (XXVIII) is evidence that a double bond plays a part in the Skraup process (Herschmann, Ber., 1908, 41, 1998)



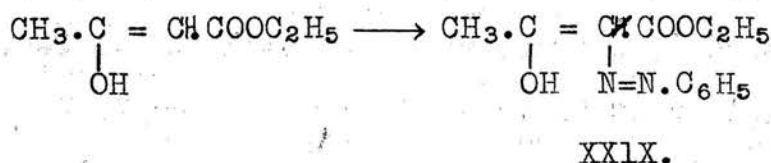
XXVII.



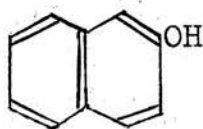
XXVIII.

More convincing evidence of bond fixation to give the Erlenmeyer structure has been obtained by other methods (for excellent summaries see Fieser, Gilman's Organic Chemistry, Vol. 1, p. 52. Baker, Annual Reports, 1936, 279). It is impossible in a short space to do justice to all the work in this field, and we content ourselves by considering in some detail evidence obtained from the coupling of substituted β -naphthols with diazonium compounds (in the author's opinion this provides the best evidence for the existence of fixed structures): Fries's work on the comparison of naphthalene and o-divinylbenzene; and Baker's work on chelation.

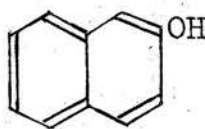
The coupling of diazonium compounds with hydroxylic compounds is known to depend on the presence of a double-bond attached to the carbon atom attacked. For example, acetoacetic ester readily forms an azo-compound (XXIX) (V. Meyer and Ambuhl, Ber., 1876, 9, 384).



In other words, a compound containing the >C=C- fragment couples with a diazonium compound. Now β -naphthol couples only in the 1-position, clearly showing the presence of a double bond between C_1 and C_2 , and the absence of a double bond between C_2 and C_3 (XXX)

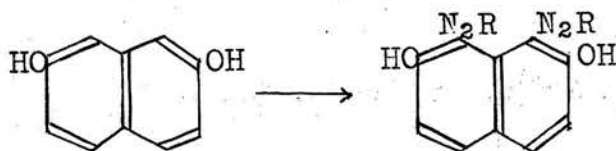


XXX.



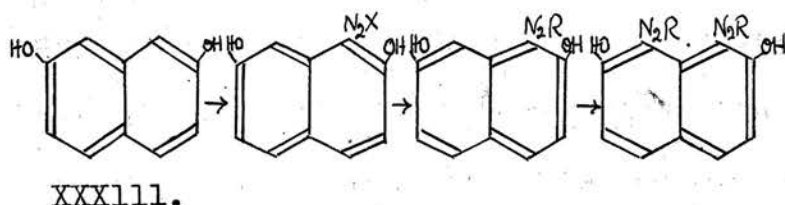
XXXI.

Fieser and Lothrop (J. Amer. Chem. Soc., 1935, 57, 1459) pointed out, however, that one of the unsymmetrical forms (XXXI) contains the necessary enolic grouping. They therefore applied more stringent tests. Ruggli and Courtin (Helv., 1932, 15, 160) showed that 2:7-dihydroxynaphthalene (XXXII) couples in the 1- and 8-positions, a reaction most readily explained by the Erlenmeyer formula

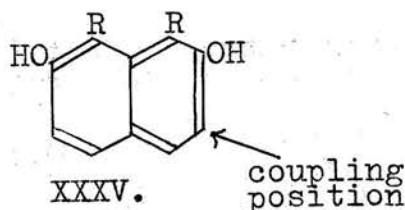
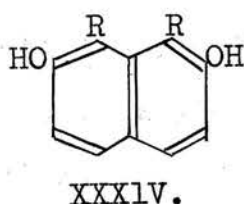


XXXII.

Fieser and Lothrop pointed out that the reaction might be explained by assuming an unsymmetrical formula (XXXIII) and migration of the double bonds during the coupling process

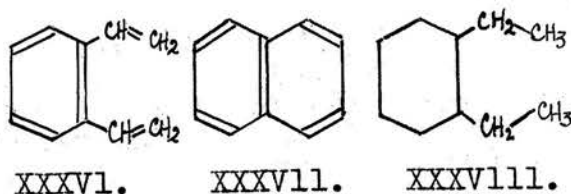


They settled the matter by investigating the action of diazonium salts on 1:8-dialkyl-2:7-dihydroxynaphthalene (XXXIV) or (XXXV).

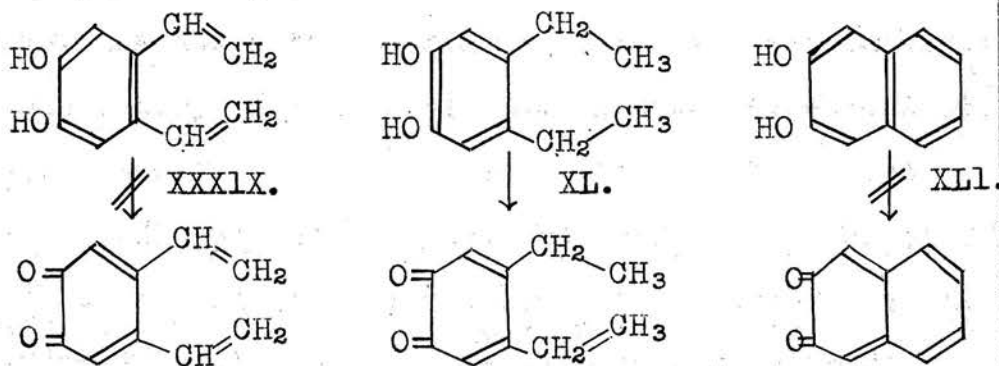


In spite of all efforts no coupling occurred, even when very active diazonium compounds were used. This result appeared to provide conclusive evidence for the Erlenmeyer formula.

Fries and Bestian (Ber., 1936, 69, 715) prepared o-divinylbenzene (XXXVI) and compared its properties with those of naphthalene (XXXVII). The absorption spectra curves were found to be strikingly similar and differed from that of o-diethylbenzene (XXXVIII).



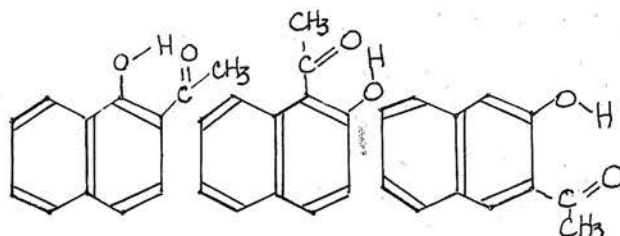
Similar results were obtained by reactivity measurements and the authors concluded there must be a close relationship between the bond arrangement in o-divinylbenzene and naphthalene. The authors (Annalen, 1937, 533, 72) strengthened their argument that the divinyl compound would tend to draw one of the nuclear double bonds into conjugation by showing that whilst dihydroxydiethylbenzene (XL) readily yielded a quinone, the corresponding divinyl-compound, like 2:3-dihydroxynaphthalene (XLI), did not give any sign of quinone formation. This is easily understandable when it is realised that quinone formation can occur only when the two hydroxy-groups are separated by a double bond



Marckwald (loc. cit.) was the first to point out that non-formation of the naphthalene quinone is probably due to the dihydroxy-compound lacking the necessary double bond system (e.g., XLII)



Baker (J., 1934, 1680) advanced the theory that chelation might lead to bond fixation in certain benzene derivatives and also applied his theory to some hydroxy-acetylnaphthalenes (Baker and Carruthers, J., 1937, 479)



All the above compounds, however, were found to be highly chelated, the chelation of the third compound being unexpected. The authors therefore hesitated to draw any definite conclusions. (It should be noted that the idea of chelation in compounds, such as the above, has now been superseded by an explanation based on the theory of resonance: see Annual Reports, 1936, 284). Baker's work has been criticised by Bonino (Ber., 1938, 71, Abt. A, 129) who correlates the properties of such hydroxyacetyl-compounds with structural symmetry. The determination of the position of double bonds in aromatic compounds by Baker's method is therefore not feasible.

The structure of naphthalene has also been studied by measurements such as those of dipole moments (Hampson and Weissberger, J., 1936, 393), optical activity (Gasoczyk and Susko, Bull. Acad. Polonaise, 1935, A, 349), and dissociation constants (Bergmann and Hirschberg, J., 1936, 331). The interpretation of such results in so

far as they apply to bond distribution is attended by many difficulties.

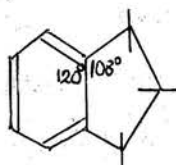
Summarising, it may be said that there is considerable evidence that naphthalene has the fixed structure represented by the symmetrical Erlenmeyer formula.

Hydrindene.

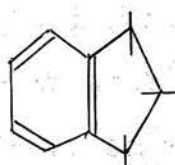
The fine structure of this hydrocarbon was first studied by Mills and Nixon (J., 1930, 2510). These investigators considered the valency angles in the system



and made the plausible assumption that the angle between the single bonds is normal, i.e., 109.28° (α). The angle which the single bonds make with the plane of the double bonds (β) is therefore 125.16° . It is then clear that formula XLVI involves less strain than formula XLVII :



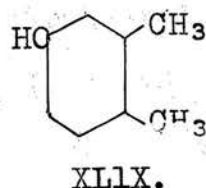
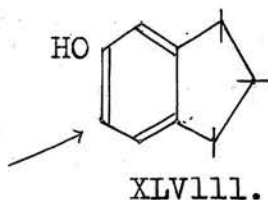
XLVI.



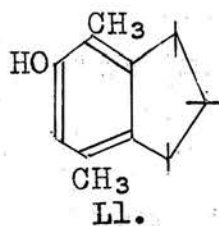
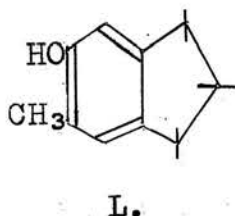
XLVII.

since the angle of an unstrained five-membered ring is 108° and that of a hexagon 120° . Mills and Nixon concluded that the fusion of a five-membered ring to a benzene ring in hydrindene results in stabilisation of

one of the Kekulé forms (XLVI). Chemical evidence supported this, bromination and diazo-coupling of 5-hydroxyhydrindene (XLVIII) occurring chiefly in the 6-position.



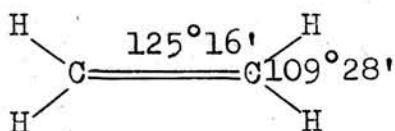
The force of this evidence is weakened by the fact that asym.-o-xlenol (XLIX) reacts similarly. Fieser and Lothrop (J. Amer. Chem. Soc., 1936, 58, 2050) avoided this difficulty by studying the properties of the compounds L and LI



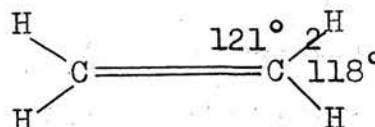
Their results supported the Mills-Nixon theory, as the first compound failed to couple with diazotised p-nitraniline, whereas the second compound readily formed an azo-compound. 5-Hydroxy-6-methylhydrindene, however, was later found to couple in weakly alkaline solution (Fieser and Lothrop, J. Amer. Chem. Soc., 1937, 59, 945) and the authors then concluded that there is no rigid fixation of bonds in hydrindene, but that the Mills-Nixon formula represented a preferred structure. This was supported by the work of Lothrop (J. Amer. Chem. Soc., 1940, 62, 132) on the intramolecular

transformation of the allyl derivative of 5-hydroxy-6-methylhydrindene to yield 5-hydroxy-6-methyl-4-allyl-hydrindene.

Arnold and Evans (J. Amer. Chem. Soc., 1940, 62, 556) pointed out that the theoretical basis of the Mills-Nixon theory must be suspect, as their model of ethylenic compounds does not agree with recorded observations. For instance, Thomson (Trans. Far. Soc., 1939, 35, 697) has shown that the bond angles in ethylene are 118° and 121° .



Mills and Nixon



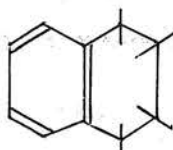
Thomson

In spite of this, the Mills-Nixon picture of hydrindene was supported by the important work of Sidgwick and Springall (J., 1936, 1532). It was shown that on the assumption of no bond fixation, o-dibromobenzene and allied compounds should have dipole moment of 2.13 D. This was found to be the case with dibromo-o-xylene, but 5:6-dibromohydrindene had a moment of 1.78, a value close to that calculated on the Mills-Nixon hypothesis. The balance of evidence is therefore in favour of this ingenious theory. A recent paper by Long and Fieser (J.A.C.S., 1940, 62, 2670) gives further evidence of

form XLVI as the "preferred" form of hydrindene.

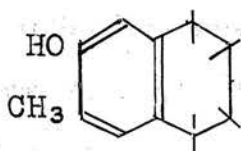
Tetralin.

Mills and Nixon (*loc. cit.*) applied their theory to tetralin and concluded, though less emphatically than in the case of hydrindene, that tetralin has structure LII.

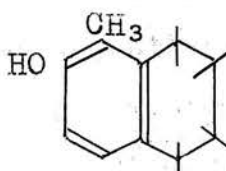


LII.

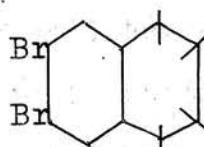
Fieser and Lothrop, on the contrary, obtained evidence indicating no fixation, as both 7-methyl-6-hydroxytetralin (LIII) and 5-methyl-6-hydroxytetralin (LIV) coupled with diazonium salts.



LIII.



LIV.



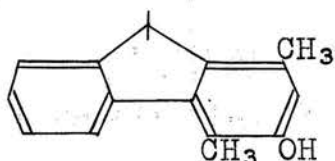
LV.

The dipole moment of 6,7-dibromotetralin was found to be 2:3 (Springall and Sidgwick, *loc. cit.*). This supports the conclusions of Fieser and Lothrop.

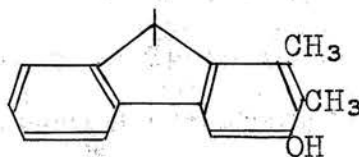
Fluorene.

Fluorene has not been so exhaustively studied as some of the other hydrocarbons (cf. The Chemistry of

Fluorene, Rieveschl and Ray, Chem. Reviews, 1938, 23, 287) but a number of workers have investigated its fine structure which is linked with its stereochemical form (cf. Cook and Iball, Chem. and Industry, 1936, 55, 467). Lothrop (J. Amer. Chem. Soc., 1939, 61, 2115) has recently given a short critical survey of the problem and shows that the evidence is often contradictory. It has the preferred structure LVI_a (Hughes, Le Fèvre, and Le Fèvre, J., 1937, 202).

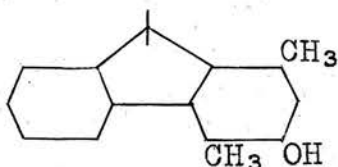


LVI a.

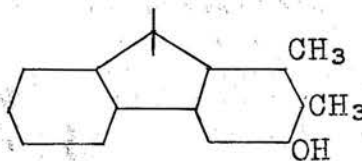


LVI b.

This formula accounts for the fact that 2-substituted fluorenes frequently undergo further substitution in the 3- but not in the 1-position. Lothrop (loc. cit.), however, has shown conclusively that there is no bond fixation. For instance, both compounds LVII and LVIII coupled with diazonium salts, and their allyl esters underwent smooth rearrangement.



LVII.



LVIII.

A short paper by Bergmann and Betlin (J. Amer. Chem. Soc., 1940, 62, 316) gives results confirming Lothrop's conclusions. Certain reactions of

2-hydroxyfluorene are claimed to show that both the 1- and the 3-positions are reactive, but the experimental results are unconvincing. For example, 2-acetoxyfluorene is stated to give 1-acetyl-2-hydroxyfluorene, but the only evidence is that the latter compound does not form an oxime, due, it is presumed, to steric hindrance. No proof that the 1-position is occupied is given. Further, as the authors admit, some of the analysis figures are not satisfactory. The chemical evidence, however, clearly indicates that there is no fixation of the fluorene molecule. It is probably a resonance hybrid of forms LVI A and LVI B (see also p. 30).

Diphenyl.

Diphenyl is not a condensed system of benzene rings and no fixation of bonds is to be expected.

Acenaphthene.

No work has been done on the fine structure of acenaphthene.

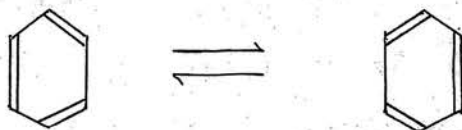
Such then are some of the developments of the pioneer experiments and theories on the structure of the aromatic hydrocarbons. Recently the problem has been attacked from a completely different point of view. The theory of resonance has been applied to the problem

and has provided a solution of some of the long standing anomalies. Further, it opens up a great field for speculation and experiment. We shall therefore consider the essential features of the theory and show how it has modified our ideas of the bond distribution in organic molecules.

The Theory of RESONANCE.

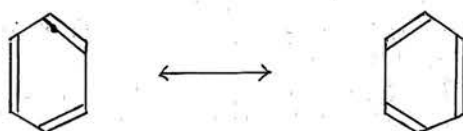
The formulae of the organic chemist are valency formulae based on fundamentals such as the quadrivalency of the carbon atom and aided by the use of symbols for single, double, and triple bonds. In spite of the comparative crudeness of these symbols the success of the resulting formulae is little short of miraculous, especially when it is found that they describe reasonably well the chemical properties of complicated compounds such as the alkaloids, vitamins, etc. The modern approach to chemical problems from the standpoint of thermodynamics and quantum mechanics, however, has shown the limitations of such formulae and of many of the older concepts. A direct outcome has been the theory of resonance, and the application of this theory to the aromatic hydrocarbons will now be considered briefly. The general theory has been accepted by most chemists and need not be detailed here (for an excellent summary, see Taylor and Brockway, Annual Reports, 1938, 196).

Kekulé regarded benzene as an oscillating mixture of the two structures (see p. 4)



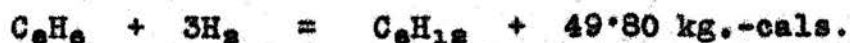
The resonance theory, however, postulates that since

these structures are equally probable, the position of the constituent atoms being identical, benzene requires both formulae to describe it. It must be stressed that benzene is not, in this theory, a mixture in any sense of the word: it is a molecular entity which has to a certain extent the properties of both Kekulé structures. In the modern terminology, benzene is a resonance hybrid with the Kekulé structures as the main contributing forms.



The theory of resonance has been accepted by organic chemists if only because for the first time it explains satisfactorily the old problem of the diminished unsaturation of benzene, etc. This is demonstrated clearly by the work of Kistiakowsky and co-workers (J. Amer. Chem. Soc., 1935, 57, 65, etc.). It was found by accurate determinations that the heats evolved on addition of hydrogen to 1 gm.-mol. of cyclohexene and benzene at 82° were 28.59 kg. cal. and 49.80 kg. cal. respectively.

Let $-x$ be the internal energy of benzene and $-y$ that of cyclohexane.



$$\text{i.e. } -x + 0 = -y + 49.80 \text{ kg.-cals.}$$

$$-x - 49.80 = -y \quad (1)$$

Suppose now that $-z$ be the energy of benzene if it consisted of 3 conjugated double bonds without any bond interaction. Then the heat of hydrogenation to cyclohexane should be three times that of the hydrogenation of cyclohexene.

$$\begin{aligned} \text{i.e. } -z + 0 &= -y + (3 \times 28.59) \\ &= -y + 85.77 \end{aligned}$$

$$\text{i.e. } -z - 85.77 = -y \quad (2)$$

Equating (1) and (2),

$$-x - 49.80 = -z - 85.77$$

$$\therefore -x = -(z + 35.97) \text{ g.-cals.}$$

The energy of benzene is therefore 36kg.-cals. less than that to be anticipated from a system of three double bonds which are not interacting. This is one of the demands of the resonance theory, namely, that the energy of a resonance hybrid is less than that of any of its constituent forms, and this decrease in energy - the stabilising or resonance energy - gives a quantitative measure of the interaction of the double bonds. In the case of benzene, so great is the interaction of the double bonds that all the C-C linkages in benzene are to be considered identical in nature with properties intermediate between those of single and double bonds.

This novel picture of benzene is in striking contrast to the older conception but it does account satisfactorily for the stability of the compound. Confirmation that the new view is essentially correct has

been obtained from two sets of observations.

(1) Spectrographic measurements have yielded information of fundamental importance regarding the structure of the simpler compounds and elements. In more complex compounds, such as organic substances, interpretation of the results is a matter of great difficulty except in the case of compounds with a high degree of symmetry. Ingold and co-workers (J., 1936, 912-971) have made use of this fortunate circumstance to study thoroughly the infra-red, Raman, and fluorescence spectra of benzene and hexadeutero-benzene. The results indicate the hexagonal symmetry of benzene as demanded by the resonance theory.

(2) Pauling was the first to point out that interatomic distances and resonance are related (Pauling, Beach, and Brockway, J. Amer. Chem. Soc., 1935, 57, 2705. See also Annual Reports, 1937, 34, 196. Penney, Proc. Roy. Soc., 1937, 158, 306). Bond lengths in organic compounds can be measured with accuracy by modern methods.

Interatomic Distances.

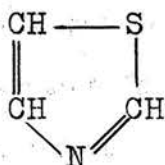
C - C	(Diamond)	1.54 Å
C = C	(Ethylene)	1.33
C ≡ C	(Acetylene)	1.20.

The C-C distance in benzene is 1.39 Å, i.e., intermediate between that of a double and single bond, and this is clearly seen if a graph is constructed in which

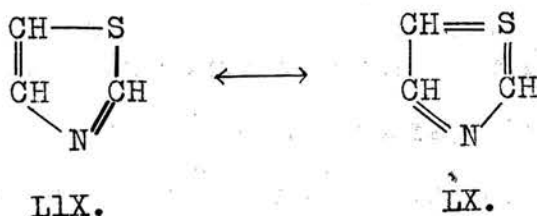
bond order is plotted against bond length. The result is in complete harmony with the resonance picture of benzene. Incidentally it may be noted that graphite with the system >C= has a double bond character of 0.33 and a C-C distance 1.42 Å. These values also correspond to a point on the curve.

The resonance picture of benzene must be accepted, and with it the conclusion that benzene and the other aromatic compounds cannot adequately be represented by any simple valency formula. The organic chemist must, of course, have some simple formulae to use in picturing and "understanding" organic compounds and their reactions. Fortunately it is permissible to resolve the benzene hybrid into its Kekulé forms, and these can be used (cf. Pauling, Gilman's Organic Chemistry, Vol. 2, p.1869), provided it is remembered that they do not represent actual molecular entities but are merely contributing structures or forms to the resonance hybrid. Throughout the thesis, Kekulé rings will be used in this sense (p.32b).

It is now necessary to enquire as to how the older structures of naphthalene, hydrindene, etc. are modified by the modern theory. Before doing so it may be pointed out that resonance appears to be one of the main attributes of aromaticity. Indeed, the theory succeeds in "explaining" the aromatic properties of certain compounds. For instance, the formula of thiazole

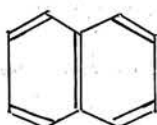


does not account for its distinctly aromatic properties. If, however, we postulate that resonance is one of the criteria of aromaticity, then we attribute that property to thiazole by ascribing to it the contributing forms LIX and LX :

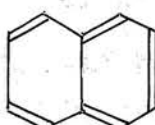


This has been experimentally verified by Erlenmeyer (Helv., 1938, 21, 863 and 1017). Many other instances will doubtless be found to occur.

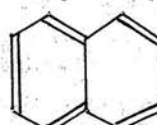
Naphthalene is undoubtedly a resonance hybrid with a resonance energy of 74.6 kg.-cals and the three unexcited structures (LXI, LXII and LXIII) as the main contributing forms (Pauling and Wheland, J. Chem. Physics, 1933, 1, 362. Pauling and Sharman, *ibid.*, 1933, 1, 606. Sherman, *ibid.*, 1934, 2, 488. Penney, Proc. Roy. Soc., 1937, 158, 306).



LXI.



LXII.



LXIII.

Pauling, Brockway and Beach (loc. cit.) assumed that equal contributions came from the three structures (an assumption only approximately correct), and assigned to the $\alpha:\beta$ -bonds $\frac{2}{3}$ and to the $\beta:\beta'$ -bonds $\frac{1}{3}$ double bond character. Naphthalene may therefore be represented by a formula such as



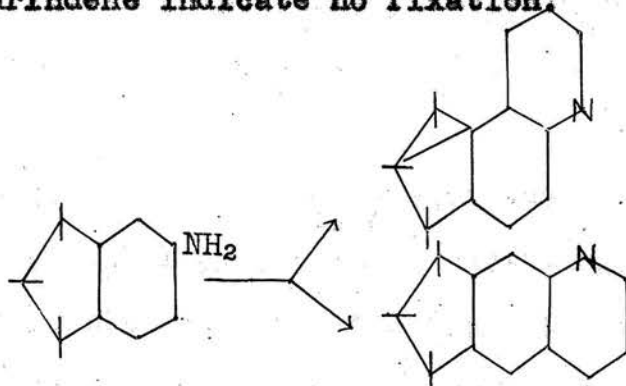
the heavy lines indicating bonds with greater double bond character (Taylor and Brockway, loc. cit.), and this may be regarded as the modern equivalent of the Erlenmeyer formula. It satisfies the requirements of the organic chemist, namely, that there is an essential difference between the $\alpha:\beta$ - and the $\beta:\beta'$ -linkages, the latter showing little sign of double bond character. The formula accounts for results such as those of Fieser and Lothrop (loc. cit.) and has certain advantages over the fixed Erlenmeyer structure, since it accounts for the substitution of some naphthalene derivatives in position-3 (see p. 8). For many purposes the Erlenmeyer formula may be used, provided it is clearly understood that it is not a fixed structure.

Kistiakowsky and co-workers (loc. cit.) found that the heat of hydrogenation of hydrindene is 45.80 kg.-cals - a value little different from that of benzene. The

resonance energy is thus 37.4 kg.-cals and there can be no doubt that hydrindene is a resonance hybrid.



This, although in disagreement with the older theory of Mills and Nixon, is in harmony with the results of other workers (p. 16). Sutton and Pauling (Trans. Faraday Soc., 935, 31, 939) have computed that a slight predominance of A (6%) is sufficient to account for the chemical properties of hydrindene and its derivatives. The results of Lindner, Sellner, Hofmann and Hager (Monats., 1939, 72, 335) on the Skraup reaction with 5-aminohydrindene indicate no fixation.



The main difficulty arising from the resonance picture of hydrindene is the apparent conflict with the dipole measurements already mentioned (p. 17). No satisfactory explanation has as yet been given.

With other aromatic compounds the results of physical measurements and chemical experiments are in agreement, i.e., a definite resonance energy is found

on the one hand, and no evidence of bond fixation on the other. The following table gives the resonance energies of several hydrocarbons already discussed (taken from the results of Pauling and Sherman, loc. cit.).

Resonance Energies in Volt-Electrons.

Acenaphthene	...	3.07
Naphthalene	...	3.24
Fluorene	...	0.71
Diphenyl	...	0.35

Summarising, it may be said that with many aromatic hydrocarbons such as fluorene, there is no chemical or physical evidence of bond fixation: that in others, such as naphthalene, the extreme view of bond fixation must be modified in terms of the theory of resonance.

There can be little doubt that the theory of resonance, by and large, must be accepted, if only because in precise mathematical terms it gives an answer to many of the organic chemist's problems. It must be stressed, however, that the theory is only in its infancy. Consequently it is not surprising that its significance is not yet fully understood, nor are all its apparent implications justified. For instance, Burawoy (J.C.I., 1940, 59, 594) recently has called attention to some unwarranted applications of the theory

to conjugated systems, the single bonds decreasing in length, as predicted by the theory, without, however, a concomitant increase in length of the double bonds. This raises some fundamental points which must be clarified.

It may well be that, just as Kekulé's formula solved some problems and raised others which have since occupied the attention of the organic chemist, the theory of resonance will, in turn, solve many problems and raise others for many years to come. This is only to be expected in the field of organic chemistry where even the simple compounds are complex in comparison to the hydrogen molecule. The implications of the resonance of the hydrogen molecule may be expressed in exact mathematical form. In more complex cases the necessary equations are obtained only after making arbitrary assumptions and approximations. It is safe to say, however, that the resonance theory "has come to stay" and the various problems it raises will only serve to stimulate the chemist and physicist to further research.

A digression at this point may not be out of place. The concise structural formulae of the organic chemist which have served so well since Kekulé's day now seem unsatisfactory. No simple picture of compounds such as naphthalene seems permissible. Pictorial formulae are of little use in indicating important facts such as the equivalence of the C-C

bonds in benzene or the difference between the $\alpha:\alpha'$ -bonds and the $\beta:\beta'$ -bonds in the naphthalene molecule. Nevertheless the organic chemist must have his formulae and it must be one of his tasks to decide the exact value as well as the limitations of his symbols. Presumably he will meet "the disastrous results of the criticism of classical ideas" by remembering the definition of Berzelius that a formula "must give with ease a summary of that which we should observe".

It is helpful to remember the dictum of the late Sir James Walker (J., 1923, 123, 939) that formulae give good valency pictures but "imperfect representation of forces" and that "confusion of these two senses sometimes leads to erroneous reasoning". Bearing in mind Walker's plea for "the utmost obviousness of our symbols and formulae", we may still use with confidence the classical formulae of Kekulé and Erlenmeyer, provided we regard them as contributing structures to the resonance picture.

One last point. We must not expect too much from our formulae. To quote Senior (J. Chem. Educ., 1935, 12, 409), "The predictive value of structural formulae is never sufficient to establish more than a high probability". Used with judgment and experience, however, they remain one of the essential tools of the organic chemist.

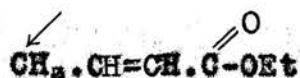
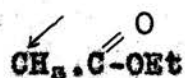
P A R T II.

During the past five years the author has investigated the fine structure of several aromatic and heterocyclic compounds.

- (1) Reactivity of halogenonitro-derivatives.
- (2) "Abnormal" Grignard reactions.
- (3) Simple substitution, such as bromination.
- (4) Absorption spectra.

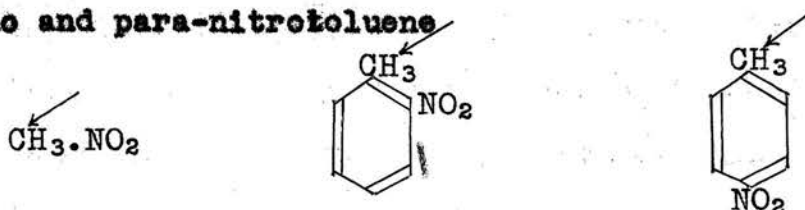
Reactivity of Halogenonitro-compounds.

It has long been recognised that the influence of one functional group on another in an organic molecule may be transmitted through a double bond or conjugated system of double bonds. For instance, the reactivity of the methyl group in ethyl acetate is also found in ethyl crotonate, the effect of the unsaturated carbethoxy-group being transmitted in the latter case by the double bond.



Fuson (Chem. Reviews, 1935, 16, 1) gave many examples of this property of the double bond under the heading "Theory of Vinylogy" and applied it both to aliphatic and to aromatic compounds. For example, the reactivity

of the methyl group in nitromethane is also observed in ortho and para-nitrotoluene



The meta-compound is inactive, as there is not the necessary double bond system between the methyl and nitro groups.

By analogy the bromine reactivity of ortho- and para-bromonitrobenzene is due to the presence in the ring of the necessary double bonds.

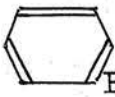
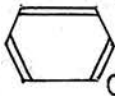




Such reactivity accordingly affords a method for determining the position of double bonds in aromatic hydrocarbons; or more correctly, the position of those bonds with greater double bond character than the others. The method has the advantage over others such as the Skraup reaction and diazo-coupling used for the same purpose, in that it is non-competitive. That is to say, in any given compound the bromine is reactive or non-reactive towards piperidine, etc., whereas with the other reactions the problem is one of which course the reaction will take. For example: does β -naphthol couple in the α - or β -position? Such results may be

interpreted as due to the greater reactivity of one position compared to the other (cf. Sutton and Pauling, loc. cit.). It is one of the merits of Fieser's work that he used compounds which overcome this difficulty.

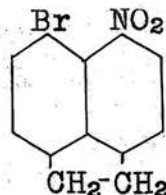
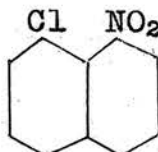
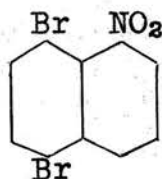
Confirmation of Fuson's Vinylogy Theory.

The halogen reactivity of four halogeno- ω -nitro-styrenes is given below.

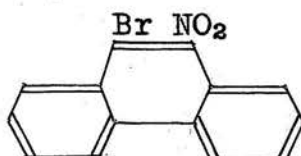
	% Bromine removed.	
	24 hrs.	48 hrs.
 <chem>BrC1=CC=C(C=C1)C=CC(=O)O</chem>	34	
 <chem>ClC1=CC=C(C=C1)C=CC(=O)O</chem>		13
 <chem>ClC1=CC=C(C=C1)C=CC(=O)O</chem>		0
 <chem>ClC1=CC=C(C=C1)C=CC(=O)O</chem>		8

The results clearly confirm Fuson's theory.

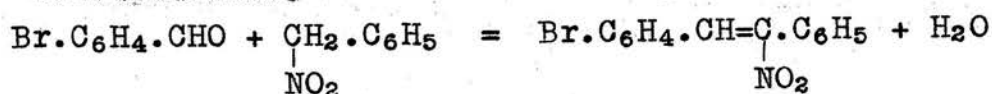
Further confirmation is obtained from the observation that the following compounds show no bromine reactivity.



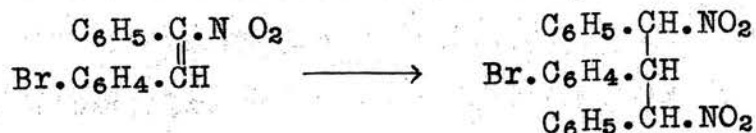
The halogeno- and the nitro-groups in these compounds are in many respects comparable to those in ortho-compounds, but the mere proximity is insufficient to produce halogen reactivity without the necessary bond system. 9-Bromo-10-nitrophenanthrene is reactive, as the C₉-C₁₀ bond is undoubtedly a double bond.



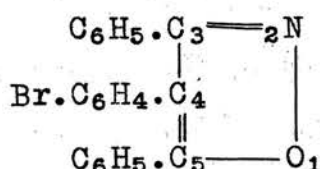
Attempts were made to prepare 2-bromo- and 4-bromo-7'-nitrostilbene for reactivity measurements, but the desired compounds were not obtained. Instead, diphenylbromophenyl-iso-oxazoles were obtained. It is to be noted that the exact structure of these compounds is not known and depends on the mechanism of formation (Heim, Ber., 1911, 44, 2016. Ruggli and Hegedus, Helv. Chim. Acta, 1939, 22, 405). In all probability the first stage is the formation of bromo-7'-nitrostilbene.



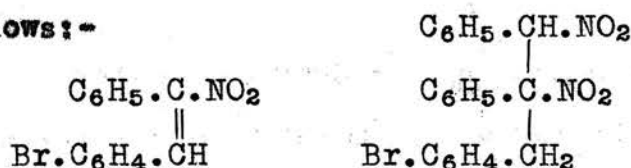
The second stage involves addition of a further molecule of phenylnitromethane to the double bond. Heim postulates addition in the following manner:



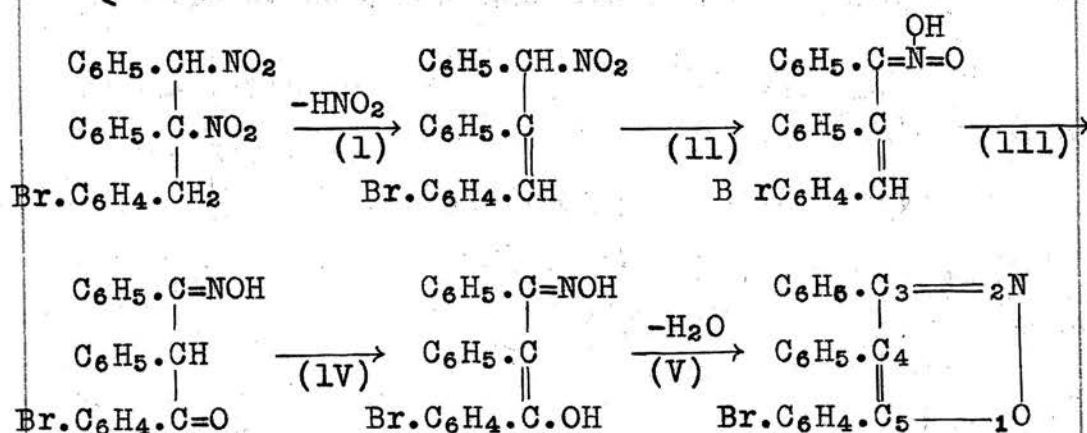
Water and nitrous acid are then lost giving 3:5-diphenyl-4-bromophenyl-iso-oxazole



Ruggli's mechanism is different and he postulates addition of phenylnitromethane to the initial product as follows:-



The iso-oxazole formation is then represented by the following series of reactions.



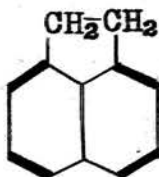
The product is on this theory 3:4-diphenyl-5-bromophenyl-iso-oxazole. The relative merits of the two theories cannot yet be assessed, but one stage of Ruggli's series, namely III, seems improbable.

Work is in progress to determine the structure of the iso-oxazoles obtained by us and hence to settle which of the above mechanisms is correct.

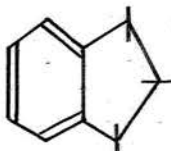
Structure of Naphthalene, Hydrindene, etc.

Reactivity measurements were made on some thirty halogenonitro-derivatives of naphthalene, etc. and the results were published in two papers (McLeish and Campbell, loc. cit.; Campbell, Anderson and Gilmore, loc. cit.). It is only necessary here to summarise these results.

- (1) There exists a pronounced difference between the $\alpha:\beta$ and the $\beta:\beta'$ bonds in naphthalene.
- (2) Evidence is strong that this difference is due to the greater double bond character of the $\alpha:\beta$ -bonds compared with the $\beta:\beta'$ -bonds.
- (3) Acenaphthene has the same fine structure as naphthalene.



- (4) In hydrindene the following structure makes the greater contribution to the resonance hybrid.



The evidence submitted, however, is not so clear-cut as in the case of naphthalene.

(5) No conclusion can be drawn from the data on tetralin derivatives.

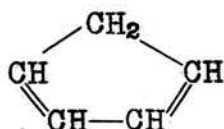
(6) Fluorene is a resonance hybrid of the forms -



(7) In diphenyl derivatives the benzene nuclei appear to be independent entities: e.g., a nitro-group in one ring does not influence a halogen atom in the other.

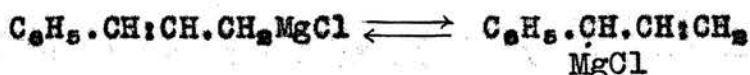
(8) The presence of the methyl group decreases the halogen reactivity in the bromonitrotoluenes.

It may be noted that in the course of these researches a serviceable colour test for fluorene and substituted fluorenes was found, and the colour test of Lippmann and Pollak for aromatic hydrocarbons was further investigated (Levy and Campbell, J., 1939, 1442). The former test is also given by cyclopentadiene, and affords evidence for LVI B as one of the contributing forms to the resonance hybrid.

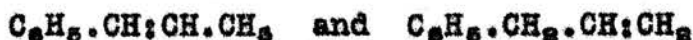


"Abnormal" Reactions of Aromatic Grignard Compounds.

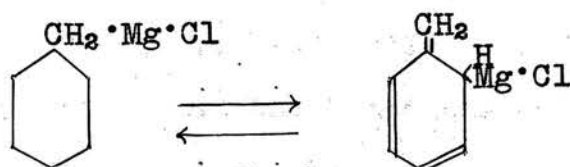
Grignard compounds prepared from unsaturated halogeno-compounds yield unexpected products. For instance, cinnamyl chloride appears to form a tautomeric mixture (Young, Ballou, and Nozaki, J. Amer. Chem. Soc., 1939, 61, 12)



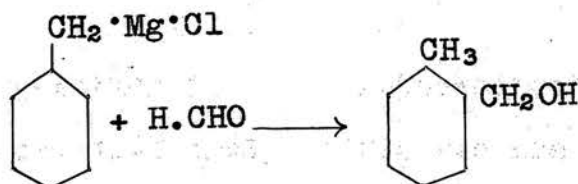
and reacts with water to form a mixture of the unsaturated hydrocarbons



In the same way, the Grignard reagent of benzyl chloride may be pictured as the tautomeric mixture



There is a considerable diversity of opinion as to the mechanism of the process but that need not concern us here. The main point is that "abnormal" reaction products may be expected from the system - $\text{CH}:\text{CH}\cdot\text{CH}_2\text{Cl}$. Thus benzylmagnesium chloride with formaldehyde yields o-methyl-benzyl alcohol



Such reactions therefore may be used to find the position of double bonds in aromatic compounds. In the case of benzyl chloride, both Kekulé forms will have the requisite double bond system, but in naphthalene it is to be anticipated that similar changes will occur much more readily with the $\alpha:\beta$ -bonds than with the $\beta:\beta'$ -bonds.

It was therefore decided to study the products obtained by the interaction of α - and β -naphthylmethylmagnesium chloride (bromide) and acetyl chloride which is one of the reagents known to give rearranged products. No rearrangement, however, was found, the products being hydrocarbons to which were assigned the formulae of 1:3-dinaphthyl-2-methylpropylenes (Campbell, Anderson, and Gilmore, J., 1940, 819). Professor J. W. Cook kindly suggested that the compounds were probably the symmetrical dinaphthylethanes. A comparison of the melting-points of our compounds and those quoted in the literature strengthens this viewpoint.

1:2-Di- α -naphthylethane 161-2°C.

1:2-Di- β -naphthylethane 182°C.

(not 253°C. as stated by Bamberger
and Lodter, Ber., 1888, 21, 54)

Our compounds melted at 162-163° and 184-185° respectively.

The whole question is being reinvestigated. It may be pointed out that analysis figures are of little value in distinguishing between these substituted ethanes and propylenes.

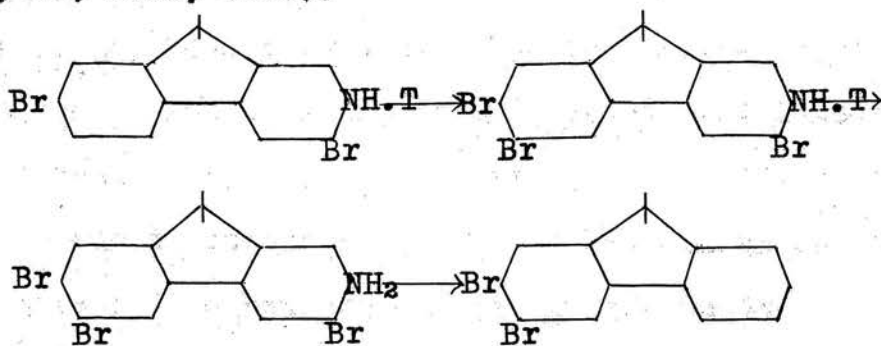
Bromination of Fluorene.

The 2- and 7-positions in fluorene are the most reactive and consequently compounds such as 2:7-dibromofluorene are readily obtained. It is therefore easily understandable why attempts to obtain substituents in position 1 have so far been unsuccessful (e.g., Eckert and Langecker, J. pr. Chem., 1928, 118, 277). In view of the fact that fluorene is a resonance hybrid (p. 30) it was thought that some of the trisubstituted fluorene might have the substituents in the 1:3:7 positions. This, however, was found not to be the case.

Bromination of 2-acetamidofluorene was shown to yield the 3:7-dibromo-compound. By hydrolysis and diazotisation of the resulting amine, 2:3:7-tribromofluorene was obtained. This was identical with the tribromofluorene obtained by Schmidt and Bauer (Ber., 1905, 38, 3765) by bromination of fluorene. The 3-position is clearly much more reactive than the 1-position.

Bromination of p-toluenesulphonamido-compounds in pyridine frequently yields di-ortho-compounds (Bell, J., 1932, 2732). For instance, b-p-toluenesulphonaphthalide gives 1:3-dibromo-b-p-toluenesulphonaphthalide. Accordingly it was thought that by bromination of 3:7-dibromo-2-p-toluenesulphonamido-fluorene, bromine might be 'forced' into the 1-position. A tribromo-compound

was obtained (Gilmore, Thesis, Edinburgh 1940) but unfortunately the orientation of the compound has not yet been accomplished owing to the fact that a reagent suitable for hydrolysing the compound to the amine has so far not been found. Until this obstacle is overcome the position of the third bromine will probably not be determined. Once the amino-compound is obtained the orientation of the compound should not be difficult. For instance, if substitution has occurred in position-6 (a distinct possibility) 2:3-dibromofluorene would be obtained by the following series of reactions, use being made of the fact that bromine ortho to the amino-group is readily removed with stannous chloride and hydrochloric acid (Franzen and Stauble, J. pr. Chem., 1921, 101, 58. Nicolet and co-workers, J. Amer. Chem. Soc., 1921, 43, 2081, etc.).

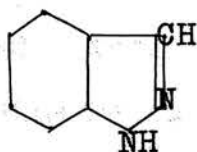


The final product would be easily synthesised from 3-nitro-2-aminofluorene (Eckert and Langecker, loc.cit.).

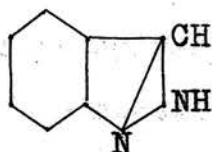
Structure of Indazole Derivatives.

Many heterocyclic compounds are condensed ring systems and consequently may be expected to possess resonance structures. This has already been proved in many cases (e.g., Pauling and Sherman, J. Chem. Phys. 1933, 1, 606), and one instance has already been cited (p. 26).

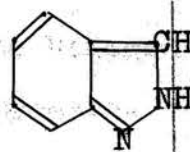
It should be possible to study the fine structure of heterocyclic compounds by the methods used for the aromatic hydrocarbons, and one compound, indazole, has been thoroughly investigated by the author and co-workers (Barclay, Campbell and Dodds, J., 1941, 113). The structure of this compound has puzzled chemists and has been intensively studied by Auwers (1919-1935). No satisfactory picture of the indazole molecule, however, has been obtained. In the light of recent developments it can scarcely be doubted that indazole is a resonance hybrid. The main contributing forms will be due to resonance of the benzene rings but the structure of the heterocyclic ring remains to be determined. The possible contributing forms are -



LXLV.

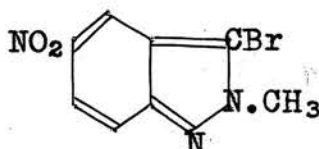


LXV.



LXVI.

Form LXV has little appeal to the organic chemist owing to the obvious strain in such a model. Form LXIV presents no difficulties, but the o-quinonoid structure LXVI is not apparently in harmony with the properties of indazole such as its stability and lack of colour. It may be mentioned in this connection that anthraquinone in the pure state is colourless (Hückel, Lehrbuch der Chemie, p. 522). We have shown, however, that at least one indazole derivative, 3-bromo-5-nitro-2-methylindazole (LXVII) possesses



LXVII.

a quinonoid structure, as only this form accounts for the observed reactivity of the halogen towards piperidine in marked contrast to the other isomers. It is therefore quite probable that other 2-alkylindazoles possess this structure and that a similar form contributes to the resonance hybrid of the parent indazole.

The 1-alkylindazoles beyond dispute have structure LXIV, and absorption spectra measurements show that this is the main contributing structure in the 3-bromo-nitroindazoles. This is in agreement with the halogen reactivity measurements, the reactivity of 3-bromo-5-nitroindazole being small. It is dangerous to argue

by analogy and apply conclusions regarding the bromo-nitroindazoles to indazole itself, but our results suggest that indazole has as its principal contributing form structure LXIV. This is in agreement with the conclusion of Auwers (Annalen, 1937, 527, 291).